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THE KINETICS AND THERMODYNAMICS OF THE DIELS-ALDER REACTION BETWEEN ANTHRACENE AND MALEIC ANHYDRIDE

BY

DONALD BRUCE DAHM

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Department of
Chemistry, South Dakota State
College of Agriculture
and Mechanic Arts

August, 1961

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THE KINETICS AND THERMODYNAMICS OF THE DIELS-ALDER REACTION BETWEEN ANTHRACENE AND MALEIC ANHYDRIDE

This thesis is approved as a creditable, independent investigation by a candidate for the degree, Master of Science, and is acceptable as meeting the thesis requirements for this degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

Head of the Major Department

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DBD

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STATEMENT OF PROBLEM

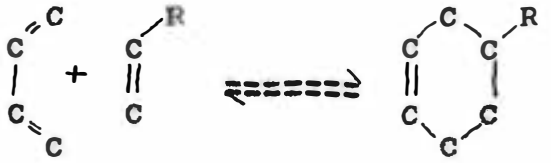
Since the first kinetic study of a Diels-Alder reaction in 1933 (75), numerous kinetic investigations of the reaction have been reported. The literature now contains a wealth of kinetic data on the general reaction.

In the last decade, a particular interest has been shown in the kinetic studies of the Diels-Alder reaction employing anthracene and its derivatives. Quite independently, anthracene and similar compounds have been studied from a standpoint of their photochemical properties and their applications to solid state physics and related fields. Such investigations have increased our knowledge of the photochemical reactions of these compounds and it has been repeatedly demonstrated that auto-oxidation and dimerization will occur under a variety of conditions (9,10,11). It is rather unfortunate that the majority of the kinetic studies involving anthracene and its derivatives have not taken into account these possible side reactions.

The purpose of this study is to reinvestigate the kinetics of the reaction between anthracene and maleic anhydride in view of the recent knowledge and to compare the results with data obtained previously.

THE DIELS-ALDER REACTION

The Diels-Alder reaction, commonly known as the diene synthesis, is a well-known example of 1:4 addition. One of the reactants, known as the dienophile, contains a double or triple bond usually activated by additional unsaturation in the α or β position; while the other reactant, which is called the diene, refers to a molecule containing conjugated double bonds. The product of the addition reaction of a dienophile with a diene is called the adduct. According to Norton (62), the majority of Diels-Alder reactions can be classified under one of the following categories:

A. 

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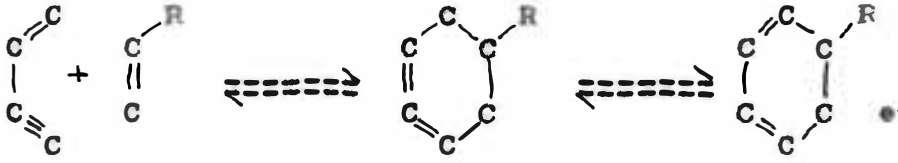
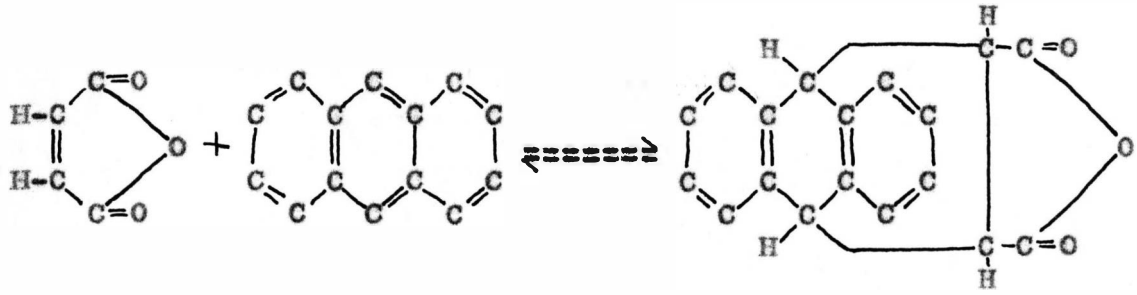
C. 

where R in the above examples is usually an electron-attracting group of some type.

The reaction under consideration in this study, the addition of anthracene to maleic anhydride to form cis-9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride, is an

example of the class A reactions.



Isolated examples of diene additions appear in the literature of the last century. Zincke and his co-workers (89,90,91,92) discovered, and later correctly formulated, the dimerization of tetrachlorocyclopentadienone. In the present century, Euler and Josephson (32) recognized the nature of the addition product of isoprene to p-benzoquinone. These observations, however, remained uncorrelated until Diels and Alder (20) demonstrated the versatility of the reaction in 1928. Their continued studies of the reaction won for them, in 1950, the Nobel Prize in Chemistry. For a complete bibliography of Diels and Alder's work covering the period from 1925 to 1951, the reader is referred to a review article by Olsen (63).

As to the mechanism of the Diels-Alder reaction, the crucial question is that of the geometrical configuration of the transition state. Three configurations, which may be distinguished as the linear, the planar, and the non-planar configurations have been proposed.

The concept of a linear transition state involves the assumption that the diene and dienophile approach end-wise to form a diradical, which then cyclises to form the product. This mechanism was first suggested by Kistiakowsky and Ransom (50). They calculated the entropy of the proposed transition state from estimated moments of inertia and vibration frequencies, thereby arriving at a calculated entropy of activation which compared favorably with experimentally determined Arrhenius frequency factors. Wassermann (83) took exception to their calculations and showed that a mathematical approach based on a non-planar transition state also gave agreement with the experimental data; hence it was impossible to validate the mechanism in this manner.

A mechanism involving a planar transition state was suggested by Evans and Warhurst (33,34) in order to calculate the electronic energy of the transition state. They proposed that the transition state involved a resonance problem similar to that of the benzene molecule. In order to verify the proposed mechanism, Rubin and Wassermann (66) instituted a kinetic study and found the results obtained could not be explained on the basis of the mechanism of Evans and Warhurst.

Currently, the most plausible explanation as stated by Ettlinger and Lewis (31) is to regard the transition state as non-planar as proposed earlier by Wassermann. This is further substantiated by some recent studies (8,77,87) that

completely rule out Kistiakowsky's proposed mechanism, i.e., the diradical concept, on the basis of thermodynamic calculations. However, these studies also indicate that a two-stage mechanism may be a possibility. Certainly, further work seems to be in order, before a definite conclusion can be made.

Concerning the electronic character of the transition state, Bergmann and Eschinazi (7) remarked on the heightened reactivity which is displayed by the dienophile, when its ethylenic double bond is conjugated with a "resonance promoting" group, such as carbonyl. This effect does not arise because electrons must be fed into and through the dienophile in one direction; for a carbonyl group at each end makes the dienophile even more reactive. The effect of substituents in the diene was also illustrated through some experiments of Hudson and Robinson (43), who used styrenes as compounds in Diels-Alder additions.

The transition state, whatever it may be, is probably attained by an initial, rapid, ionic reaction involving electron transfer from the diene to the dienophile. The second and what is believed to be the rate-determining step is a rearrangement of the transition state to yield the adduct (51).

In 1936, Littmann (55), while studying the polymerization of α-phellandrene with maleic anhydride, noticed that a yellow color, which appeared immediately upon mixing of

the reagents, disappeared as the reaction progressed. This was assumed to be due to the formation of an ionic complex. In 1958, McKusick and Biehn (59), synthesized the first cyanocarbon, tetracyanoethylene, which has to date proven to be the most active dienophile synthesized. Diels-Alder reactions involving this dienophile have been subsequently studied and in all cases a bright color results before the precipitation of the adduct. This color was also assumed to be due to the formation of the ionic complex, but as yet this assumption has not been validated.

It has been observed repeatedly that the adducts of Diels-Alder reactions are thermally unstable (51). The reactions between maleic anhydride and a number of polycyclic hydrocarbons are truly reversible. In a study by Bachmann and Kloetzel (2), identical mixtures of the hydrocarbon, maleic anhydride, and the adduct were obtained either by heating xylene solutions of the pure adduct or the reactants in equimolar portions. This study also indicated that, in most cases, the reactions under consideration gave essentially quantitative yields.

The diene synthesis is remarkably stereo-specific. Two stereoisomers of the adduct may be envisioned, however, only one is actually formed; for the reaction always results in a cis-addition. For example, anthracene and maleic anhydride have been shown to give cis-9,10-dihydroanthracene-9,

10-endo-α,β-succinic anhydride, which on hydrolysis gives the cis-DL-acid. This cis-DL-acid loses water and forms the anhydride even on attempted recrystallization or on standing in a vacuum dessicator (3).

From a theoretical treatment, it has been shown that the endo-adduct is always formed in the diene synthesis. For comparison purposes, the addition of cyclopentadiene to benzoquinone may form two possible adducts; one corresponding to the endo-, and the other to the exo- adduct. Wassermann (79, 80, 81) has calculated the energy differences between these two configurations and the results indicate that the endo- configuration is favored by several kilocalories per mol.

The first kinetic study of a Diels-Alder reaction was performed by Wassermann in 1933 (78). The reaction studied was between benzoquinone and cyclopentadiene. The course of the reaction was followed using a colorimetric technique.

Kistiakowsky and Lacher (49) employed partial pressure measurements to determine the course of the gaseous reactions between cyclopentadiene and acrolein, isoprene and acrolein, butadiene and acrolein, and butadiene and crotonic aldehyde. Wassermann (82) also studied these same gaseous reactions and his results agreed with those obtained by Kistiakowsky and Lacher. In the same study, Wassermann also measured the bimolecular associations of acrolein, benzoquinone, cyclopentadiene, α-napthoquinone, and benzoquinone-cyclopentadiene with cyclopentadiene in benzene solutions.

In 1936, Khambata and Wassermann (47) also measured the kinetics of the inverse diene reaction in the pure state and in paraffin solutions. From the results obtained, they concluded that the mechanism was the same in both the pure state and in solution. The reaction studied was the decomposition of dicyclopentadiene. The dimerization of cyclopentadiene was also studied in the same systems and the mechanism for the bimolecular association was concluded to be the same in either phase. In 1937, Benford, Khambata, and Wassermann (5) studied the kinetics of the reactions of α-napthoquinone, benzoquinone, acrolein, and cyclopentadiene with cyclopentadiene in various phases. The first two reactions were studied in benzene solutions, while the latter two were studied in the gaseous phase.

Wassermann (65,84) then proceeded to make a considerable study of homogeneous catalysis in the diene synthesis. Generally, the diene reaction is not highly susceptible to catalysts, although it is slightly susceptible to general acid catalysis. The results that Wassermann obtained indicated that acids do accelerate the reaction in the gaseous phase and in solution, however the effect was not too large. Catalytic activity, however, increased with increasing strength of acid used. Other conclusions drawn were that any solvent used for catalysis must be non-basic and that weakly basic or neutral solutes and salts of the catalyzing acid retard the

catalytic action. Other forms of catalysis, including heterogeneous catalysis, have been described by Wassermann and workers (45,48,85) but either they are less general, or it is less apparent how they operate.

Yates and Eaton (88) studied the acceleration of several Diels-Alder reactions, including a reaction between anthracene and maleic anhydride. The solvent used in all cases was dichloromethane and the catalyst was aluminum chloride. This reaction in the presence of the aluminum chloride catalyst was 95% complete in 1.5 minutes at 0° C. Other reactions studied yielded similar results. The studies of Fray and Robinson (37) utilized catalysts of the Friedel-Crafts type also; for example, aluminum chloride, tin (II) chloride, boron trifluoride, iron (III) chloride, titanium tetrachloride, etc. It was here demonstrated that a number of Diels-Alder additions could be effected under much milder conditions than those required in the absence of such a catalyst.

Solvent effects have also been studied by many workers (6,18,19,21,35,38,39). The results indicate that the rate of reaction increases as the dielectric constant of the solvent increases.

Continuing in diene research, Eisler and Wassermann (29) considered some stereochemical factors while studying the reactions of benzoquinone with butadiene and cyclopentadiene in benzene solutions and the dimerizations of butadiene

and cyclopentadiene in the gaseous phase. Eisler and Wassermann (30) also studied the kinetics of the association of maleic anhydride and butadiene at various temperatures.

In every kinetic study, it has been shown that the forward reaction is of second-order, while the reverse reaction is of first-order. The general reaction is exothermic, so that an increase in temperature favors the decomposition of the adduct.

Maleic anhydride, which is used very often as a dienophile in the Diels-Alder reaction, has been shown to react with benzene and substituted benzenes. Keefer and Andrews (46) in 1955 postulated a possible structure of a 1:1 benzene-maleic anhydride adduct. They have since been shown to be in error. Angus and Bryce-Smith (1) in 1960 reacted maleic anhydride with benzene in the presence of ultraviolet light to form a 2:1 adduct. In 1961, Grovenstein and co-workers (40) also synthesized the same adduct and confirmed the structure postulated earlier by Angus and Bryce-Smith. Substituted benzenes will react with maleic anhydride in a like manner, as Schecter and Barker (67) obtained a product with xylene using di-tertiary butyl peroxide as a catalyst. The yields for these reactions are good, although the reactions must be initiated under forceful conditions.

The first theoretical treatment of the Diels-Alder reaction was reported by Brown (12). Of particular interest

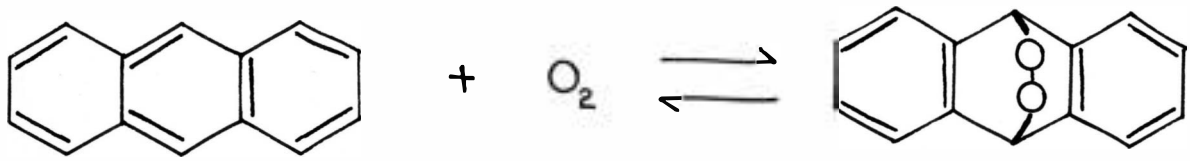
in Brown's subsequent papers (13,14,15) were the theoretical calculations of equilibrium percentages of adduct which agreed with the experimental values of Bachmann and Kloetzel (2). Later theoretical studies of the reaction include those of Basu (4) and Fernandez-Alonso and Sebastian (36).

The first kinetic study of a Diels-Alder reaction involving anthracene was performed by Krzyzaniak (52) in 1951. The temperature range employed was 100-142° C. and the dienophile used was maleic anhydride. In 1955, Keefer and Andrews (46) determined the kinetics of the reactions between anthracene and the dienophiles, maleic anhydride and chloromaleic anhydride, at slightly above room temperatures. Vaughan and Andersen, (74) subsequently studied the reactions of anthracene with alkylmaleic anhydrides and alkylfumaric acids. Their results indicated that as the length of the alkyl chain increased, the rate constant decreased.

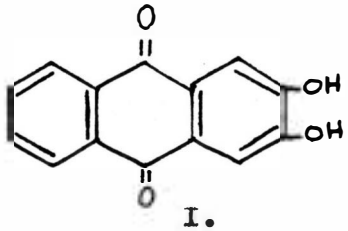
In the aforementioned studies with anthracene, no particular attention was given to the possibility that anthracene may noticeably undergo possible side-reactions, such as photochemical auto-oxidation and dimerization. Such reactions are not limited to anthracene, however, as it has been shown that anthracene derivatives also undergo the above reactions to a greater or lesser degree (11,12,13). If these side-reactions occur to an appreciable extent, it is rather obvious that the concentration of the diene in respect to

time will not represent a true kinetic study of the Diels-Alder reaction. Since most kinetic studies of Diels-Alder reactions are conducted by following the change in concentration of the diene, the kinetics of the reaction under consideration will not be accurate.

The photochemical reactions of anthracene and its derivatives are non-chain reactions yielding simple products, the transannular peroxides (42)



Under certain conditions, however, other products may be formed. Voyatzakis and his co-workers (75,76) have isolated alizarin (I), azulene (II), anthraquinone (III), chrysene, (IV), and quinizarin (V) from anthracene



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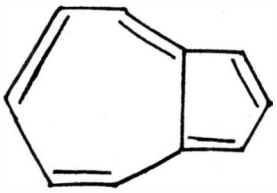

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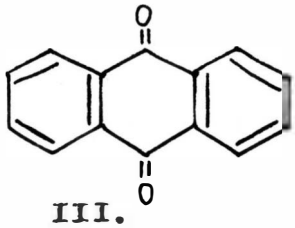

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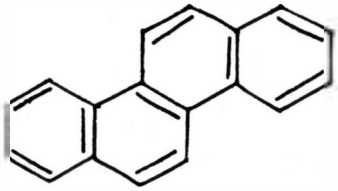

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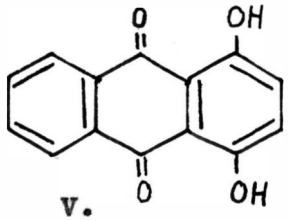

V.

absorbed on variously treated silicas which were illuminated with ultraviolet light. No possible mechanisms were postulated. This study may have resulted from earlier work by Roberts, Barter, and Stone (64), who demonstrated that anthracene oxidation to its transannular peroxide was catalyzed by silica in the presence of oxygen.

The transannular peroxide of anthracene is most easily formed when anthracene is dissolved in carbon disulfide and exposed to ultraviolet light. This reaction occurs simultaneously with the photodimerization of the anthracene. The formation of the dimer is favored in concentrated solutions of anthracene in alcohol, benzene, or acetone; while the peroxide is preferrentially formed in dilute carbon disulfide solutions. The peroxide can be recovered from the solution as a crystalline compound that explodes at 120° C. (22,23,24).

Lalande and co-workers have made extensive studies on photopolymerization in the meso-anthracene series (16,53,54). The results have indicated that the dimers formed have the trans-configuration, which the authors presume is the configuration of the anthracene dimer also. The mechanism that they set forth provides for a polar transition from reactant to product in diffidence to a radical mechanism.

Dufraisse and co-workers (25,26,27) discovered that the ultraviolet absorption spectra of the photo-oxide and of the maleic anhydride adduct of anthracene are both similar

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to that of 9,10-dihydroanthracene, but very different from that of anthracene itself. They also discovered that meso-alkyl groups on the anthracene molecule greatly facilitate the photochemical addition of oxygen. 9,10-dimethylanthracene readily forms a photo-oxide, even in the ordinary light of the laboratory. The effects of some other meso-substituents have been studied, and, in general, the presence of meso-substituents of the meta-directing type either inhibit or entirely prevent the reaction.

There have been many postulated mechanisms for the dimerization and photochemical auto-oxidation of anthracene and its derivatives (17,56,57,69,70,71,86). At the present time there is not one which is entirely satisfactory. All of the above mechanisms, however, indicate that light does transform anthracene and its derivatives into dimers and peroxides, but further work is required before a completely satisfactory mechanism can be postulated. Further detailed information on the photochemistry of the above substances can be found in a recently published symposium (42).

Experimental evidence resulting from the investigation of the Diels-Alder reaction has shown that the above conditions of photo-oxidation and dimerization do exist. Simons (68), in 1960, demonstrated that light and oxygen greatly catalyze the reaction between anthracene and maleic anhydride. Duncan (28), while studying the kinetics of the reaction

between maleic anhydride and 9,10-dichloroanthracene, showed that dissolved gases in the solvent used had a marked effect on the change in concentration of diene employed.

SYMBOLS

In order to clarify the text, the following list of symbols are included. For the most part, the symbols used in this paper are those recommended by the IUPAC, American convention.

AB^*	concentration of the activated complex
a_s	absorbency index of the sample
A_s	absorbency of the sample
b	cell length
c	concentration of an absorbing species
C	concentration of a reaction entity
C_a	concentration of reactant A or diene
C_{ab}	concentration of adduct
C_b	concentration of reactant B or dienophile
e	base of natural logarithm
$\underline{e}$	average energy of vibration
ΔE_a	energy of activation
ΔE°	change in standard state internal energy
f	subscript to indicate the forward reaction
ΔF°	change in standard state free energy
h	Planck constant
ΔH°	change in standard state enthalpy
k	reaction rate constant
k'	Boltzmann constant
K	thermodynamic equilibrium constant

κ	transmission coefficient
ln	natural logarithm of
n	order of reaction
o	subscript on concentration, indicates initial time
$\Delta(PV)$	change in pressure-volume product
r	subscript to indicate the reverse reaction
ΔS^o	change in standard state entropy
t	reaction time
T	absolute temperature
T_s	transmittancy of the sample
T_{soln}	transmittancy of the solution
T_{solv}	transmittancy of the solvent
v	frequency
x	amount of reactant that has reacted in time t
*	superscript pertaining to the activated complex
Z	rate of passage over the potential energy barrier

DISCUSSION OF REACTION KINETICS AND THERMODYNAMICS AS APPLIED TO THE PROBLEM UNDER CONSIDERATION

Every chemical reaction takes place at a definite rate depending upon the experimental conditions. The most important of these conditions are the concentrations of the reacting substances, temperature, the presence of a catalyst, and radiation. Some reactions are so rapid that they appear to be instantaneous, while others are very slow at the temperature under such consideration. Between these two extremes are the reactions whose rates can be conveniently studied in the laboratory. It is the study of the rates of chemical reactions and the influence of the various experimental conditions on the reaction rate which constitutes the field of reaction kinetics.

The discussion which is to follow will primarily be concerned with mathematically developing a system which is directly applicable to the reaction under consideration in this problem, namely a Diels-Alder reaction. The treatment which follows can be found in almost any standard physical chemistry text such as Moore (61).

For a reaction

$$A + B \longrightarrow \text{products} \qquad (1)$$

the defining differential equation for the order n of a reaction may be expressed as

$$-\frac{dC}{dt} = k\,C^{n} \qquad (2)$$

if all the reactants are in equimolar concentrations initially. The order of the reaction n can either be an integral whole number or a non-integral ration of small whole numbers.

The integration of equation (2) results in two different solutions. The general solution obtained is

$$\frac{1}{C^{n-1}} = (n-1)\,kt + \frac{1}{C_o^{n-1}} \qquad (3)$$

while the other, with n equal to one, is applicable to first-order reactions only.

$$\ln C = -kt + \ln C_o \qquad (4)$$

Upon examining equation (3) it can be seen that a plot of $1/C^{n-1}$ against time which results in a straight line, has a slope equal to $(n-1)k$ and an intercept equal to $1/C_o^{n-1}$. From equation (4) it can also be seen that if a plot of ln C against time results in a straight line, the reaction is of order one having a slope of $-k$ and an intercept of $\ln C_o$.

If the reactants in equation (1) are not in equimolar concentrations initially, equation (2) would take the form

$$\frac{dx}{dt} = k\,(C_a - x)\,(C_b - x) \qquad (5)$$

for a second-order reaction. Upon integrating equation (5) by the method of partial fractions and rearranging

$$\ln \frac{(C_a - x)}{(C_b - x)} = k(C_a - C_b)t - \ln \left(\frac{C_b}{C_a} \right) \quad (6)$$

A plot of $\ln (C_a - x)/(C_b - x)$ against time results in a straight line with a slope equal to $k(C_a - C_b)$ and an intercept of $-\ln C_b/C_a$. The second-order rate constant, k, can easily be calculated from this expression.

The mathematical description of reaction rates thus far has been confined to a few particular types, but it should not be concluded that most chemical reactions are amenable to such simple mathematical treatment. Cases of real chemical interest are usually complex, and the exact analysis difficult. More often than not, two or more different reactions are taking place at the same time so that the mathematical description of the over-all reaction is the resultant of several different expressions. The important complications are consecutive, reverse, and competing reactions.

The rate of any chemical reaction may also be formulated in terms of its activated complex. The rate of the reaction is simply the number of activated complexes passing per unit of time over the top of the potential-energy barrier. This rate is equal to the concentration of the activated complex times the average velocity with which the complex moves across the barrier to the product side.

$$- \frac{dC_a}{dt} = AB^* \; Z \qquad (7)$$

It makes no difference how these complexes are formed, or how many intermediate stages there may be between the reactants and the activated complex.

Consider the following reaction,

$$A + B \rightleftharpoons (A\,B)^* \longrightarrow \text{products} \qquad (8)$$

If the activated complex is in equilibrium with the reactants, the equilibrium constant for the formation of the complex is

$$K^* = \frac{AB^*}{C_a \; C_b} \qquad (9)$$

and the concentration of the complex is

$$AB^* = K^* \; C_a \; C_b \qquad (10)$$

The rate of passage over the barrier, Z, is equal to the frequency with which the complex flies apart to form the products. The complex flies apart when one of its rotational degrees of freedom becomes a vibrational degree of freedom, and what was originally one of the bonds holding the complex together becomes simply the lines of center between the separating fragments. The frequency, v, is equal to $\underline{e}/h$ where $\underline{e}$ is the average energy of the vibration that results in the decomposition of the products. Since the assumption of this

is a thoroughly excited vibration at the temperature T, it has a classical energy of

$$\underline{e} = k'T \tag{11}$$

and the corresponding frequency becomes

$$v = \frac{k'T}{h} \tag{12}$$

The reaction rate can then be expressed as

$$- \frac{dC_a}{dt} = k\, C_a\, C_b = K^*\, C_a\, C_b\, \frac{k'T}{h} \tag{13}$$

and hence the rate constant is

$$k = \frac{k'T}{h} K^* \tag{14}$$

This is the general expression given by the transition-state theory for the rate constant of any elementary reaction. To be more precise, however, the left-hand side of equation (14) should be multiplied by a factor of χ, the transmission coefficient, which is the probability that the complex will dissociate into products instead of back into reactants.

A thermodynamic formulation of equation (14) can also be given by introducing the standard free energy change

$$\Delta F^{o*} = - RT \ln K^* \tag{15}$$

where ΔF^{o*} is the difference between the free energy of the

activated complex and that of the reactants, when all are in their standard states. In this system the standard state has been taken to be the state of unit concentration, because rate constants are usually expressed in terms of concentrations. Since,

$$\Delta F^{o*} = \Delta H^{o*} - T\Delta S^{o*} \tag{16}$$

equation (14) becomes

$$k = \frac{k'T}{h} e^{-\Delta F^{o*}/RT} = \frac{k'T}{h} e^{\Delta S^{o*}/R} e^{-\Delta H^{o*}/RT} \tag{17}$$

or rearranged

$$\ln k = \ln \frac{k'T}{h} + \frac{\Delta S^{o*}}{R} - \frac{\Delta H^{o*}}{RT} \tag{18}$$

The Arrhenius equation states

$$\frac{d \ln k}{dt} = \frac{\Delta E_a}{RT^2} \tag{19}$$

Now ΔH^{o*} is almost equivalent to the experimental energy of activation ΔE_a in equation (19). This can be shown by differentiating equation (18) with respect to T and substituting the result into equation (19). This yields

$$\frac{\Delta E_a}{RT^2} = \frac{\Delta H^{o*} + RT}{RT^2} \tag{20}$$

and hence

$$\Delta E_a = \Delta H^{o*} + RT \qquad (21)$$

The above mathematical treatment may be applied to the Diels-Alder reaction, provided that the forward and reverse reaction rate constants can be evaluated. In the Diels-Alder reaction under consideration, the reaction, neglecting the activated complex for the sake of simplicity, can be represented as

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} AB \qquad (22)$$

In this system, the kinetic expression assumes the form

$$-\frac{dC_a}{dt} = k_f C_a^{n_f} - k_r C_{ab}^{n_r} \quad \text{where } C_a = C_b \qquad (23)$$

Assuming that the reaction proceeds almost to completion, the second term on the right-hand side of equation (23) will be negligible by comparison to the first term until a large portion of the reactants has disappeared. Under these conditions, equation (23) reduces to a form of equation (2) which can be satisfactorily used for the evaluation of the reaction order and the rate constant for the association of AB.

For the reverse reaction the use of equation (23) is expected to be much more difficult. By regulating experimental

procedures, however, it is possible to arrive at a single expression which may be used. Starting with a pure solution of AB, the first term on the right-hand side of equation (23) has a value of zero initially. In the case of most Diels-Alder reactions, k_f is usually much larger than k_r. Even under these conditions, the first term will be negligible by comparison to the remaining terms during the very early stages of the reaction. Utilizing these parameters, equation (24) will also reduce to a form of equation (2),

$$\frac{dC_a}{dt} = k_r C_{ab}^{n_r} \qquad (24)$$

Theoretically, equation (24) could be used to evaluate the order of the dissociation of AB much the same as equation (2) is used to evaluate the order of the association of AB. In the system under consideration, however, this is not the case as the concentration change of AB per unit of time is very small and C_{ab} exp n_r remains essentially constant for any plausible reaction order. Until the term $k_f C_a$ exp n_f becomes important, equation (24) could be represented as

$$\frac{dC_a}{dt} = k_r (C_o)_{ab}^{n_r} \qquad (25)$$

or after integration between the limits of zero and time t

$$(C_a)_t = k_r (C_o)_{ab}^{n_r} t \qquad (26)$$

Under these conditions n_r cannot be determined from kinetic data alone and in order to evaluate n_r, the thermodynamic equilibrium constant for ideal solutions must be employed,

$$K = \frac{k_f}{k_r} \qquad (27)$$

By ideality it is assumed that in dilute solutions the values of the activity coefficients of the various non-ionic species under consideration are unity. Utilizing the value for k_f obtained from the experimental application of equation (2) and the determined value of the thermodynamic equilibrium constant evaluated from the reaction mixture at equilibrium, an approximate value of k_r may be calculated from equation (27) and then compared with the values of k_r obtained using equations (3) and (4) assuming different values of n_r. The value of k_r thus calculated from equation (27) that most nearly corresponds to one of the assumed k_r values calculated from either equation (3) or equation (4) will then determine the order of the dissociation of AB.

The standard state increase in free energy at various temperatures may be calculated from the equation

$$\Delta F^{\circ} = -RT \ln K \tag{28}$$

Using the definition

$$\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{29}$$

for an isobaric, isothermal system, equation (28) may be rearranged to give

$$K = e^{-\Delta F^{\circ}/RT} = e^{-\Delta H^{\circ}/RT} e^{-\Delta S^{\circ}/R} \tag{30}$$

or

$$\ln K = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{31}$$

A plot of ln K against 1/T which results in a straight line will have a slope of $-\Delta H^{\circ}/R$ and an intercept of $\Delta S^{\circ}/R$. By definition

$$\Delta H^{\circ} = \Delta E^{\circ} + \Delta(PV) \tag{32}$$

In liquid solutions where $\Delta(PV)$ is negligible, ΔH° is approximately equal to ΔE°.

In the type of system which has been developed, all of the thermodynamic quantities will be evaluated through the use of the thermodynamic equilibrium constant. The accuracy of these values will never be more reliable than the computed value of the thermodynamic equilibrium constant.

SPECTROPHOTOMETRY

Spectrophotometry may be considered as the study of the relative measurement of radiant energy as a function of wavelength. The term relative should be stressed since in spectrophotometry, the radiant energy transmitted or reflected by a system is nearly always measured, not in absolute units, but as related to some standard such as the solvent in which the substance being analyzed is dissolved.

Consideration of the kinds of compounds which may be studied quantitatively brings in the concept of chromophoric grouping. Originally, as the name implies, this concept was applied to colored substances; for it had been found that the presence of color could be related to the presence in the molecule of certain atomic groupings which caused absorption bands in the visible spectrum. This same term has been retained for groupings which lead to formation of absorption bands in the ultraviolet region of the spectrum, even though these bands produce no visible effect.

In both the visible and ultraviolet regions of the spectrum, which extend from a wavelength of about 200 millimicrons to about 400 millimicrons for the ultraviolet region, and from about 400 to 700 millimicrons for the visible, the mechanism which accounts for the absorption bands is similar. In both regions the absorption of radiation is caused by the transfer of the energy of that radiation to electrons in the

outer orbit of the molecule which then undergo displacement. In the ultraviolet region the energy involved in this displacement is greater than in the visible region, but qualitatively the displacements are of the same type.

The prevalent technique in spectrophotometry involves the passage of radiation comprising a restricted range of wavelengths through a liquid confined between the windows of a cell. The ratio of the radiant energy leaving the cell containing the solute to that incident on the cell is most often designated as $T_{soln.}$, while the corresponding ratio for the cell containing the pure solvent is represented by $T_{solv.}$, then

$$T_s = \frac{T_{soln.}}{T_{solv.}} \tag{33}$$

and by definition

$$A_s = -\log_{10} T_s = \log_{10} \frac{1}{T_s} \tag{34}$$

At the basis of al quantitative absorption measurements are two laws: Bouguer's law relating absorptive capacity and thickness of the absorbing medium, and Beer's law relating absorptive capacity and concentration of a solute in a solution. The former states that each layer of equal thickness of a homogeneous absorbing medium absorbs an equal fraction of the radiant energy passing through it. Beer's law states that the absorptive capacity of the solute is directly

proportional to the concentration of the solute. The two laws may be combined to yield the expression

$$A_s = a_s\, b\, c = -\log_{10} T_s \qquad (35)$$

Whenever it is applicable, concentrations of the solute may be calculated from equation (35) which rearranged gives

$$c = \frac{A_s}{a_s\, b} \qquad (36)$$

The units in which b and c are expressed should always be specified as should the temperature of the sample during measurement.

The problem is now the determination of a single absorbing substance in the absence of other constituents with interfering absorptions. From the absorbancy curve of the substance being determined, the best wavelength at which to make the absorption measurement for its determination should be decided upon. Usually, this will correspond to an absorption maximum, since the curve flattens out there so that a small error in setting the wavelength scale on the spectrophotometer will not introduce a significant error in the transmittancy value.

When the most appropriate wavelength has been chosen at which to make the measurement, it is then necessary to test for adherence to Beer's law at the wavelength. This

may be done by plotting absorbancy against concentration and observing whether or not the plot is a straight line. If it is not, Beer's law does not hold over the concentration range plotted. Even if a straight line is not obtained for the entire concentration range tested, it may be true for a limited range of concentrations.

In this discussion thus far, no consideration has been given to the instruments which will provide the spectrophotometric data. The author will make no attempt to discuss the optics and mechanics of various spectrophotometers, but will instead describe the general features of most commercially-produced instruments.

Spectrophotometers are instruments which measure transmittancies over an extended wavelength region of the spectrum at narrow wavelength intervals. Regardless of the type of instrument, they all have in common the following fundamental parts: (1) a source of radiant energy, (2) a prism or a grating to produce dispersion of mixed radiation containing energy of various wavelengths so that so-called monochromatic radiation, actually narrow-wavelength regions, may be isolated before passage through a sample; (3) a device for holding the sample of which the absorbancy is to be measured, which makes possible the simultaneous or consecutive measurement of absorption in the sample and in a reference medium; and (4) a device for detecting and measuring radiant

energy either visually or by means of electric currents produced by the effect of the energy upon an appropriate photoelectric cell.

In this study, The Beckman Quartz Spectrophotometer, Model DU, is being used. In this instrument light from a source of radiant energy is focused on a slit by means of a system of mirrors. The light entering the slit is collimated by a mirror and passes through the quartz prism and reflects back along nearly the same path through a slit and through the sample or sample compartment. After passage through the sample compartment, the beam of light is incident upon a photomultiplier tube. By rotating the prism through various angles, the desired wavelengths can be obtained. For further information concerning specific spectrophotometric methods, the reader is referred to Mellon (60).

EXPERIMENTAL PROCEDURES

A Beckmann Quartz Spectrophotometer, Model DU, equipped with a photomultiplier attachment and a cell compartment maintained at a temperature of 25° C. was used to follow the change in concentration of one of the reacting substances, namely anthracene, which was undergoing a Diels-Alder reaction. The concentration of the anthracene was measured at various intervals of time. The wavelength scale on the spectrophotometer was calibrated using the alpha and beta lines of the atomic hydrogen spectrum.

All determinations were measured in unmatched silica cells fitted with ground-glass stoppers. Since the cells were unmatched, it was necessary to calibrate them by placing pure solvent in both cells and obtaining the difference in absorbancy in the wavelength region under consideration. The solvent used was Fisher certified reagent xylene and the wavelength region under such consideration was from 320 to 400 millimicrons.

A sample of xylene, used as a reference, was placed into one of the calibrated silica cells and the solution under consideration was placed into the other silica cell. These cells were placed in the cell compartment of the spectrophotometer. The instrument, which had been "warming up" for at least an hour to attain stability, was adjusted to the outside electrical currents from the 6-volt lead storage

battery by means of a dark current control. The balance was attained when the galvanometer needle gave minimum deflection. Radiation of a given wavelength was then passed through the cell containing the xylene, and the slit width and the sensitivity control were adjusted to give optimum sensitivity at a minimum deflection from the galvanometer needle. The second cell containing the solution was then placed in the beam of radiation, and the absorbancy of the solute was read after the calibrated transmittancy dial was adjusted to give minimum deflection of the galvanometer needle.

Spectra of anthracene, maleic anhydride, and the adduct, cis-9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride were obtained in this manner. In the spectral range of 320 to 400 millimicrons, anthracene exhibited four maxima in absorbancy at 326, 342, 359, and 378 millimicrons. It was decided that the two largest maxima exhibited by anthracene, 359 and 378 millimicrons should be used in the kinetic study. Both maleic anhydride and the adduct were transparent at these two wavelengths. Beer's law was verified to an anthracene concentration of 10.25×10^{-5} moles/liter at the two maxima.

The anthracene, Eastman number 480, used in this study was purified by sublimation before each experiment to a blue-violet fluorescence. The maleic anhydride, Matheson, Coleman and Bell number 2837, used in this study was recrystallized

twice from chloroform and then from xylene, while the adduct, which was prepared by the method of Bachmann and Kloetzel (2), was recrystallized twice from xylene. The melting points of maleic anhydride and the adduct were found to be 51 and 264° C. respectively, which agreed with the values reported in the literature. An analysis of the adduct for carbon and hydrogen was made and compared favorably with the calculated values. The purity of the maleic anhydride was ascertained using the non-aqueous titration method of Huhn and Jenckel (44) and the anhydride was found to contain a small amount of maleic acid.

In view of a possible reaction of maleic anhydride with the solvent, the stability of maleic anhydride in xylene solutions was determined in the following manner. A 2.00 X 10^{-3} moles/liter xylene solution of maleic anhydride was prepared and a portion of it placed into one of the silica cells and used as a reference. Another portion was refluxed at a rapid rate for three hours, cooled and the absorbancy measured in the spectrophotometer in the range of 320 to 400 millimicrons. No change in absorbancy of the refluxed sample was noted, thus indicating that if a compound were formed, it did not absorb in the spectral range under consideration. In the absence of peroxides and ultraviolet light, it was assumed that the maleic anhydride would not react with the solvent.

In verifying Beer's law for anthracene at the two maxima being used, reproducible results could not be obtained. This was thought to be due to the instability of the anthracene in the solvent. Hence, it was desirable to study the stability of anthracene in xylene under various conditions. The experiment was conducted as follows: Four volumetric flasks containing known amounts of anthracene were subjected to the following treatments; the first flask containing anthracene in oxygen-saturated xylene was exposed to a light source and flask two, which contained the same contents as flask one, was stored in the dark. Flask three contained anthracene dissolved in boiled xylene as did flask four. The former was subjected to a light source while the latter was stored in the dark. The light source was a one hundred watt incandescent light bulb. The absorbancies at 359 and 378 millimicrons were then measured at various times using boiled xylene in the reference cell. It was found that samples of anthracene in oxygen-saturated xylene suffered an appreciable change in concentration when exposed to light. Further experiments were conducted using solutions prepared and transferred in an atmosphere of nitrogen in order to keep the oxygen content at a minimum. Reproducible results could not be obtained when verifying Beer's law even while employing these precautionary measures.

As a result, it was decided than an investigation was necessary to determine the effect of dissolved gases on the spectrum of pure xylene. The absorbancy of xylene, saturated with nitrogen, oxygen, and helium was measured using the spectrophotometer and a sample of degassed xylene in the reference cell. The degassed xylene was obtained by freezing and thawing commercial xylene under a vacuum and using an acetone-dry ice mixture to freeze the xylene. The samples were saturated by bubbling the desired gas into the degassed xylene for a period of at least five minutes. All the samples containing the absorbed gases exhibited absorbancies in the spectral range of 320 to 400 millimicrons, with exception of helium, which exhibited a negligible absorbancy throughout the entire region investigated. In order to avoid the above tedius procedure of degassing the xylene in the preparation of each solution in the kinetic study, an alternate procedure of vigorously boiling the xylene was proposed and tested. Such a sample of xylene did not exhibit an appreciable absorbancy at 359 and 378 millimicrons when measured against the degassed xylene prepared by the method of freezing and thawing and hence, the alternate procedure was employed. All subsequent anthracene solutions were prepared and transferred in the presence of helium after reproducible results of such solutions were obtained in the verification of Beer's law.

For studying the kinetics of the forward reaction, 2.00×10^{-3} moles/liter solutions of anthracene and maleic

anhydride were prepared by weighing the desired amounts of the respective solids and dissolving them in predetermined volumes of boiled xylene. Two milliliters of both solutions were transferred by pipets with drawn-out tips into five milliliter Coby N/C glass ampoules. The air in the empty ampoules was displaced by helium which was blown in at a rapid rate. The ampoules were then sealed by fusion and lowered into a two or three liter round-bottom flask containing a refluxing liquid. At various times two or more ampoules were removed from the flask, cooled rapidly as to quench the reaction and opened. The samples were diluted with boiled xylene and the absorbancy of the anthracene solutions determined as previously described. The liquids employed and their reflux temperatures were water (100° C.), toluene (100° C.), n-butanol (120° C.), and xylene (140° C.).

At two of the temperatures, 110 and 120° C., the change in concentration of several "control samples" of anthracene was determined. This was carried out as follows. The ampoules were filled with anthracene only and the air flushed out with helium. These were then sealed as described earlier and lowered into the round-bottom flask. At various times, these samples were analyzed as mentioned previously. No change in concentration of the anthracene was noted, thus indicating that, to within the limits of experimental error, the anthracene was not suffering any side reactions.

Several rate determinations of the forward reaction using unequal concentrations of anthracene and maleic anhydride were also made in an attempt to determine the molecularity of the reaction. In the first determination, 4.00×10^{-3} moles/liter anthracene and 2.00×10^{-3} moles/liter maleic anhydride solutions in xylene were used to determine the reaction rate at 140° C., while in the second, 2.00×10^{-3} moles/liter anthracene and 4.00×10^{-3} moles/liter maleic anhydride solutions were employed at the same temperature. In addition, 4.00×10^{-3} moles/liter solutions of anthracene and maleic anhydride were prepared and the rate constant determined at 140° C.

It should be pointed out at this point that in every forward reaction studied, equal volumes of each reactant were used. Hence, the final concentration of each reactant was one-half of its initial value.

For studying the reverse reaction, a 1.00×10^{-3} moles/liter solution of the adduct was weighed and dissolved into a predetermined volume of boiled xylene. Portions of this solution were placed into glass ampoules by means of a pipet with a drawn-out tip, the air flushed out as indicated previously and then sealed by fusion. The ampoules were lowered into a round-bottom flask that was filled with a refluxing liquid. At various times, two or more of these ampoules were removed from the flask, cooled rapidly to quench

the reaction and opened. The absorbancy of the anthracene was again determined in the same manner as described above. The temperatures employed were the same as those used in the forward reaction.

The volumetric glassware used in the preparation of all solutions was calibrated using water at 25° C.

RESULTS

The spectrum of anthracene in xylene at 25° C. was obtained and found to have absorbancy maxima at 326, 342, 359 and 378 millimicrons, as shown in Table 1 and Figure I. Both maleic anhydride and the adduct were transparent at 359 and 378 millimicrons while both compounds exhibited a slight absorbancy at the other two maxima.

In this study it was found that anthracene in xylene obeys Beer's law to a concentration of 10.25×10^{-5} moles/liter at 359 and 378 millimicrons, as shown in Table 2 and Figure II.

Solutions of anthracene in xylene were found to suffer a change in concentration when exposed to light, if the xylene contained oxygen. The effects of light and dissolved gases on xylene solutions of anthracene are tabulated in Tables 3 and 4.

Xylene solutions containing various gases were found to exhibit absorbancies in the range of 320 to 400 millimicrons. The results are shown in Table 5.

The specific rate constants for the forward reaction at the four temperatures under consideration were determined by plotting the data in Tables 6-9, reciprocal diene concentration against time, and computed from the slopes of the lines obtained in Figures III-VI. The entropy of activation and energy of activation for the forward reaction were

obtained from the intercept and slope of a plot of the logarithm of the forward reaction rate constant against the reciprocal of the Kelvin temperature. The results are shown in Table 10 and on Figure VII.

Table 11 represents the data obtained for a forward reaction at 140° C. using 4.00×10^{-3} moles/liter of each reactant initially which results in the straight line, as shown in Figure VIII from whose slope the forward reaction rate constant is calculated. In Tables 12-15, the kinetic data was tabulated for the two forward reactions that were studied at 140° C. using unequal concentrations of diene and dienophile. Figures IX and X illustrate the results in graphical form. The slopes, after evaluation, yield the respective rate constants for each determination.

The specific rate constants for the reverse reaction at the same four temperatures considered in the forward reaction were determined by plotting the data in Tables 16-19, logarithm of the adduct concentration against time, and computed from the slopes of the lines in Figures XI-XIV. The entropy of activation and energy of activation for the reverse reaction were obtained from the intercept and slope of the logarithm of the reverse reaction rate constant plotted against the reciprocal of the Kelvin temperature, using the data in Table 21 and graphically presented in Figure XV.

Equilibrium constants calculated from the equilibrium mixtures are compared with provisional equilibrium constants

at 120° and 140° C., assuming that the reverse reaction is zero, first, and second-order. The results are tabulated in Table 20.

The effect of temperature on the equilibrium constant is illustrated in Table 22. A plot of the logarithm of the equilibrium constant against the reciprocal of the Kelvin temperature yields the straight line in Figure XVI. The energy of activation for the reaction is evaluated from the slope of the curve, while the entropy for the reaction is ascertained from the intercept of the same plot.

The changes in the standard state free energy are illustrated in Table 23 for the forward, reverse, and overall reactions.

All slopes and intercepts were calculated statistically using the method of least squares. The estimated errors for the experimentally determined values were obtained using standard statistical methods.

Table 1. Absorption Spectrum of Anthracene in Xylene at 25° C.

Wavelength mu	Slit width mm	Absorbancy corrected	Absorbancy index X 10^{-3} liters/mole cm
320	0.04	0.087	1.71
323	0.04	0.117	2.31
325	0.04	0.141	2.78
326*	0.04	0.143	2.82
327	0.04	0.138	2.72
331	0.02	0.110	2.17
332	0.02	0.111	2.19
333	0.02	0.116	2.29
340	0.02	0.257	5.06
341	0.02	0.278	5.48
342*	0.02	0.279	5.50
343	0.02	0.262	5.16
348	0.02	0.152	3.00
349	0.02	0.148	2.92
350	0.02	0.151	2.98
355	0.01	0.278	5.48
358	0.01	0.410	8.08
359*	0.01	0.424	8.35
360	0.01	0.400	7.88
365	0.01	0.146	2.88
367	0.01	0.110	2.17
368	0.01	0.102	2.01
369	0.01	0.107	2.11
374	0.01	0.212	4.18
377	0.01	0.357	7.03
378*	0.01	0.397	7.82
379	0.01	0.386	7.61
385	0.01	0.056	1.10

*Absorption maxima

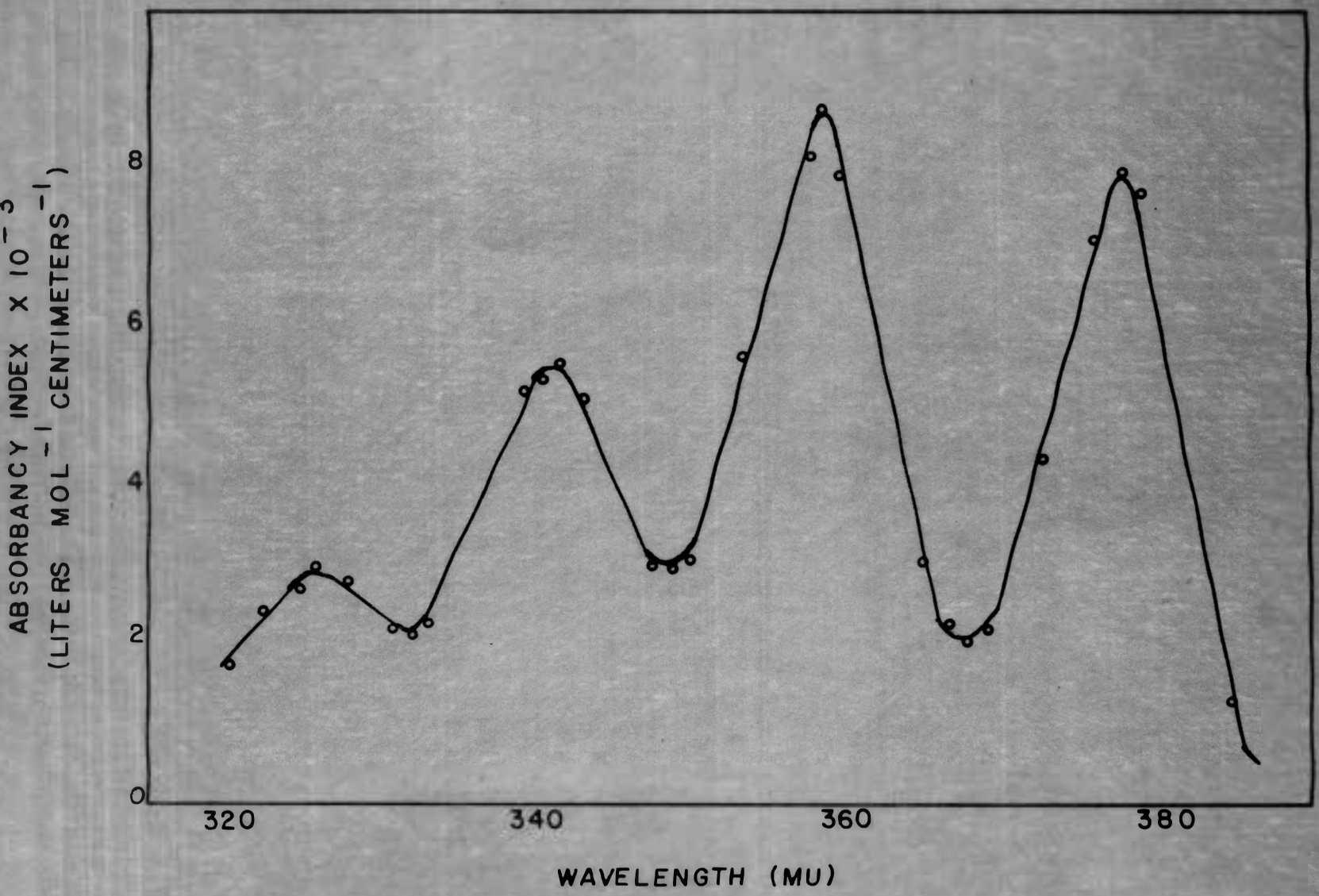

FIGURE I ABSORPTION SPECTRUM OF ANTHRACENE IN XYLENE AT 25° C.

Table 2. Absorbancy of Anthracene in Xylene at Various Concentrations at 25° C.

Anthracene concentration X 10^5 mols/liter	Absorbancy at 359 mu corrected	Absorbancy at 378 mu corrected
1.009	0.086	0.080
2.047	0.170	0.158
3.949	0.337	0.315
5.112	0.418	0.389
10.25	0.837	0.780

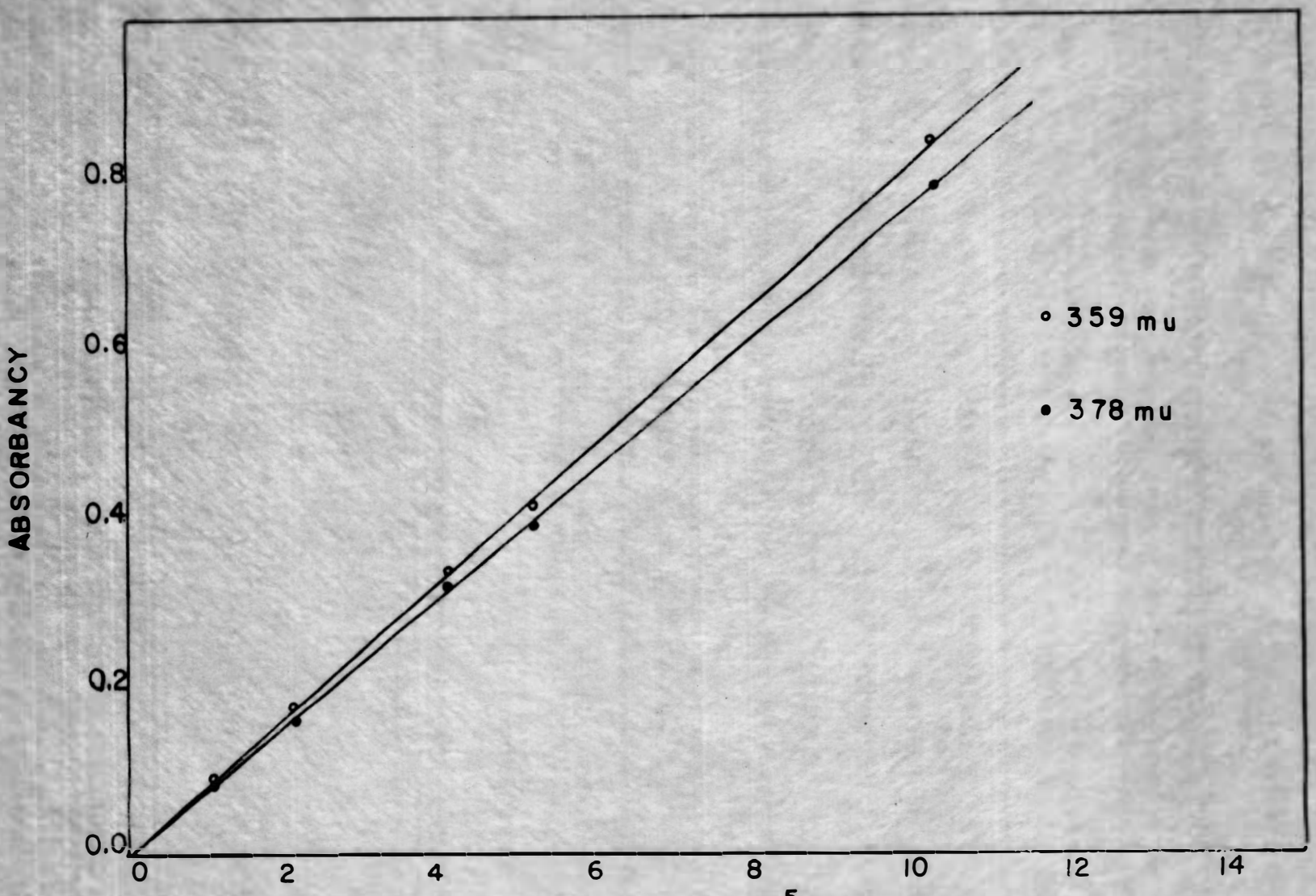

FIGURE II ABSORBANCY OF ANTHRACENE IN XYLENE AT VARIOUS CONCENTRATIONS

Table 3. Change in Concentration of Anthracene in Boiled Xylene as a Function of Time

Time hour	Solution exposed to light Concentration of Anthracene grams/liter 359 mu	378 mu	Solution unexposed to light Concentration of Anthracene grams/liter 359 mu	378 mu
0.00	2.08	2.07	2.08	2.07
28.33	2.10	2.10	2.06	2.07
76.67	2.24	2.25	2.09	2.09
100.67	2.25	2.26	2.09	2.09

Table 4. Change in Concentration of Anthracene in Oxygen-Saturated Xylene as a Function of Time

Time hour	Solution exposed to light Concentration of Anthracene grams/liter 359 mu	378 mu	Solution unexposed to light Concentration of Anthracene grams/liter 359 mu	378 mu
0.00	1.96	1.96	2.05	2.06
12.00	1.97	1.98	2.03	2.03
22.83	2.25	2.25	2.03	2.03
43.00	----	----	2.03	2.03
77.83	2.48	2.48	2.03	2.03

Table 5. Effect of Dissolved Gases on the Absorption Spectra of Degassed Xylene

Wavelength mu	Absorbancy Using Boiled xylene	Absorbancy using oxygen-saturated xylene	Absorbancy using nitrogen-saturated xylene	Absorbancy using helium-saturated xylene
320	0.006	0.196	0.113	0.001
325	0.003	0.149	0.096	-0.001
330	0.004	0.118	0.086	-0.001
335	0.003	0.094	0.080	-0.003
340	0.004	0.073	0.064	-0.003
345	0.001	0.054	0.061	-0.002
350	0.003	0.040	0.057	-0.002
355	0.002	0.027	0.050	-0.002
360	0.003	0.018	0.047	-0.001
365	0.001	0.012	0.043	-0.001
370	0.000	0.009	0.040	-0.001
375	0.000	0.007	0.040	-0.001
380	0.000	0.006	0.036	0.000
385	0.000	0.004	0.035	-0.001
390	0.000	0.005	0.034	-0.001
395	0.000	0.004	0.032	-0.001
400	0.000	0.004	0.031	-0.001

Table 6. Determination of K_f at 100° C.

Time hour	Dilution factor	Absorbancy at 359 mu	Diene concn. X 10^4 mols/l	Absorbancy at 378 mu	Diene concn. X 10^4 mols/l	Avg. Diene concn. X 10^4 mols/l	Reciprocal diene concn. 1/mol
0.00						10.0	1000
2.93	1:25	0.292	8.75	0.271	8.73	8.74	1140
3.53	1:25	0.287	8.60	0.268	8.63	8.62	1160
5.03	1:25	0.260	7.80	0.239	7.70	7.75	1290
5.03	1:25	0.258	7.75	0.239	7.70	7.73	1290
6.47	1:25	0.249	7.48	0.227	7.33	7.41	1350
6.50	1:25	0.249	7.48	0.230	7.40	7.44	1340
7.67	1:25	0.237	7.10	0.221	7.13	7.12	1400
7.80	1:25	0.232	6.95	0.214	6.90	6.93	1450
8.98	1:25	0.229	6.88	0.211	6.80	6.84	1460

k_f = 54.2 ± 3.2 liters/mol hour (from figure III)

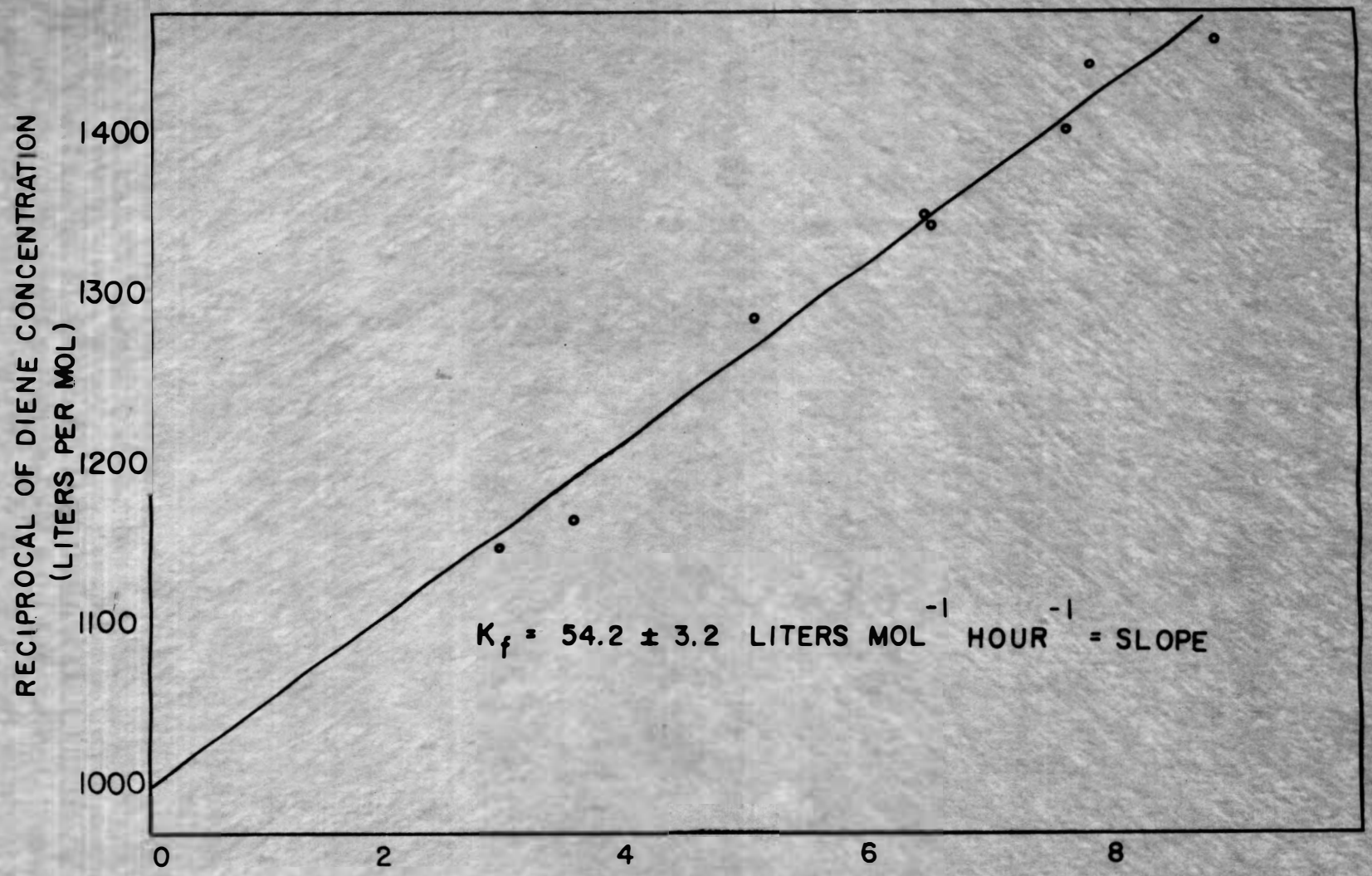

FIGURE III. DETERMINATION OF K_f AT 100° C.

Table 7. Determination of k_f at 110° C.

Time hour	Dilution factor	Absorbancy at 359 mu	Diene concn. X 10^4 mols/l	Absorbancy at 378 mu	Diene concn. X 10^4 mols/l	Avg. Diene concn. X 10^4 mols/l	Reciprocal diene concn. l/mol
0.00						10.00	1000
0.87	1:25	0.313	9.40	0.292	9.40	9.40	1060
0.90	1:25	0.313	9.40	0.294	9.47	9.44	1060
1.58	1:25	0.298	8.95	0.279	9.00	8.98	1110
1.60	1:25	0.300	9.00	0.281	9.05	9.03	1110
2.25	1:25	0.290	8.70	0.270	8.70	8.70	1150
2.25	1:25	0.292	8.75	0.270	8.70	8.73	1150
3.07	1:25	0.276	8.28	0.255	8.23	8.26	1210
3.08	1:25	0.276	8.28	0.255	8.23	8.26	1210
4.28	1:25	0.255	7.65	0.236	7.60	7.63	1310
5.45	1:25	0.242	7.26	0.227	7.32	7.29	1370
7.28	1:25	0.220	6.61	0.205	6.61	6.61	1510
7.45	1:25	0.220	6.61	0.207	6.67	6.64	1510

k_f = 67.6 ± 2.2 liters/mol hour (from figure IV)

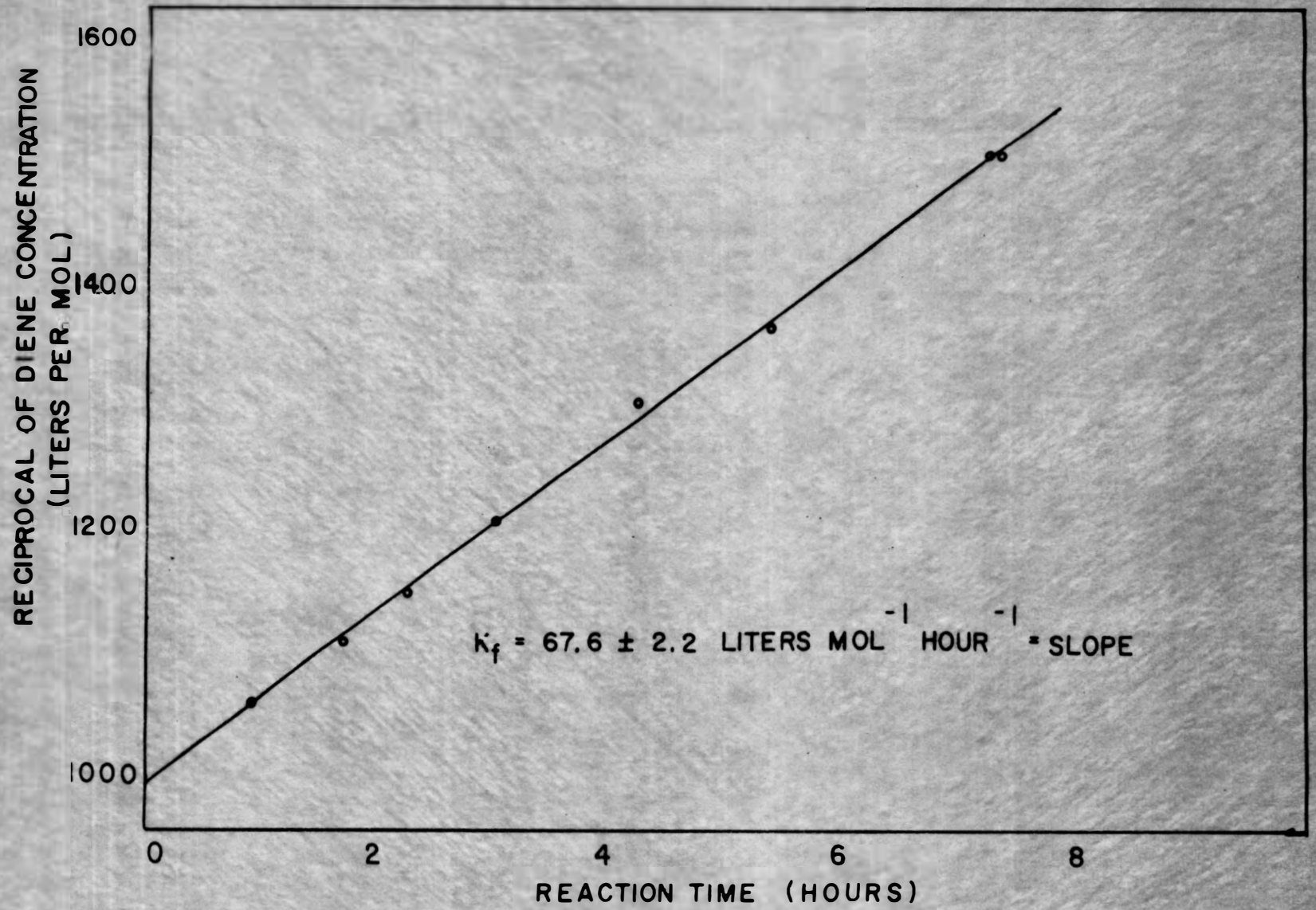

FIGURE IV DETERMINATION OF K_f AT 110° C.

Table 8. Determination of k_f at 120° C.

Time hour	Dilution factor	Absorbancy at 359 mu	Diene concn. X 10^4 mols/l	Absorbancy at 378 mu	Diene concn. X 10^4 mols/l	Avg. Diene concn. X 10^4 mols/l	Reciprocal diene concn. 1/mol
0.00						10.0	1000
0.40	1:25	0.320	9.60	0.300	9.65	9.63	1040
0.42	1:25	0.323	9.70	0.301	9.70	9.70	1030
0.97	1:25	0.304	9.13	0.284	9.15	9.14	1090
1.00	1:25	0.306	9.18	0.286	9.23	9.21	1090
1.00	1:25	0.305	9.15	0.285	9.18	9.17	1090
1.32	1:25	0.297	8.90	0.276	8.90	8.90	1120
1.38	1:25	0.296	8.88	0.275	8.85	8.87	1130
1.87	1:25	0.286	8.58	0.268	8.62	8.60	1160
1.87	1:25	0.286	8.58	0.268	8.62	8.60	1160
2.38	1:25	0.277	8.30	0.259	8.35	8.34	1200
3.02	1:25	0.262	7.85	0.244	7.85	7.85	1270
3.03	1:25	0.264	7.93	0.247	7.95	7.94	1260
3.50	1:25	0.254	7.65	0.239	7.70	7.67	1300
3.57	1:25	0.252	7.57	0.236	7.60	7.59	1320
4.12	1:25	0.247	7.40	0.231	7.45	7.43	1350
4.13	1:25	0.247	7.40	0.230	7.42	7.41	1350
4.62	1:25	0.238	7.15	0.223	7.20	7.18	1390
4.63	1:25	0.239	7.17	0.225	7.24	7.21	1390
4.90	1:25	0.232	6.95	0.214	7.00	6.98	1430
4.97	1:25	0.233	6.97	0.218	7.03	7.00	1430

k_f = 85.0 ± 2.7 liters/mol hour (from figure V)

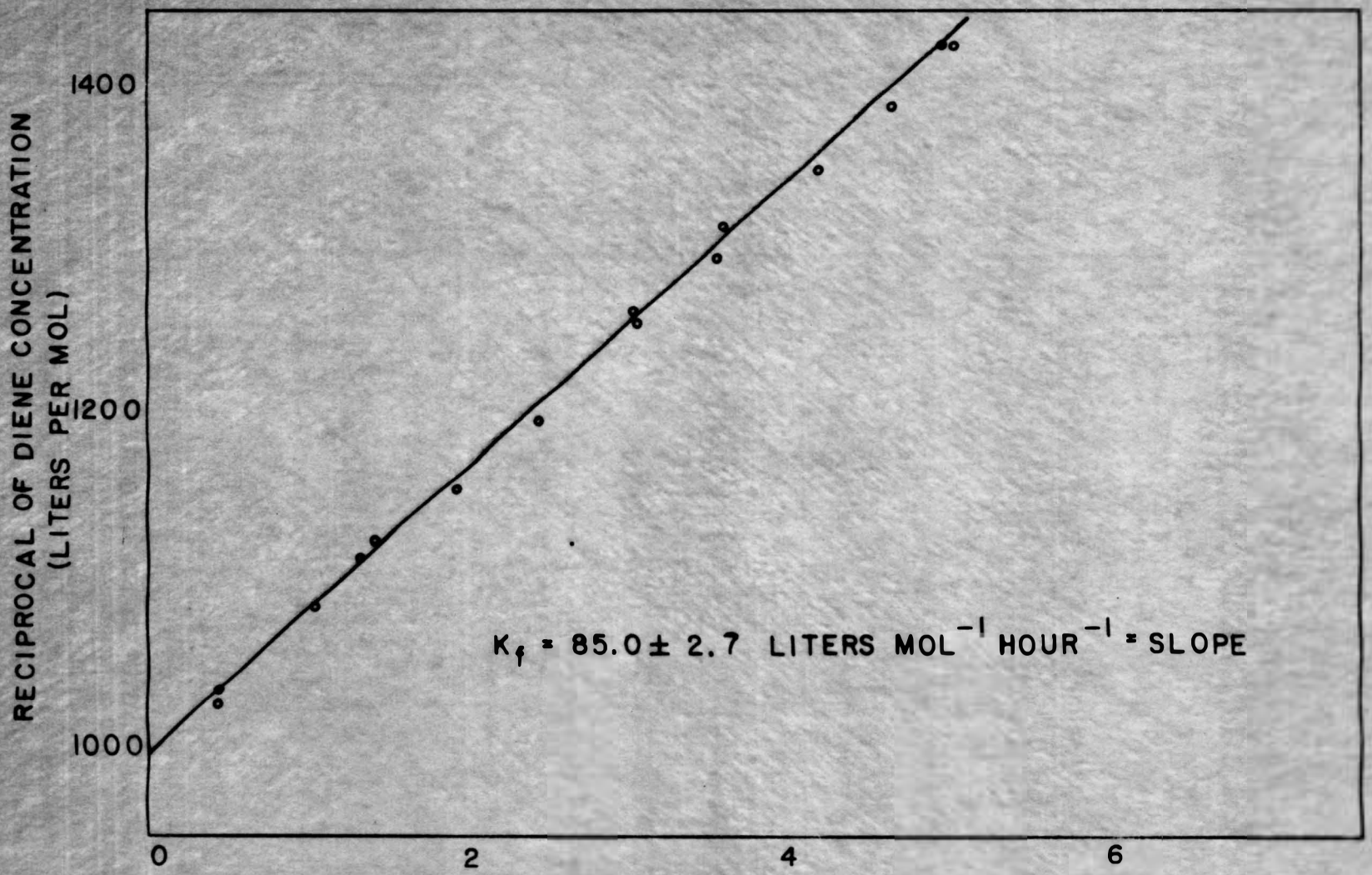

FIGURE V DETERMINATION OF K_f AT 120° C.

Table 9. Determination of k_f at 140° C.

Time hour	Dilution factor	Absorbancy at 359 mu	Diene concn. $\times 10^4$ mols/l	Absorbancy at 378 mu	Diene concn. $\times 10^4$ mols/l	Avg. Diene concn. $\times 10^4$ mols/l	Reciprocal diene concn. 1/mol
0.00						10.0	1000
0.60	1:25	0.311	9.33	0.290	9.36	9.35	1070
0.60	1:25	0.302	9.08	0.283	9.12	9.10	1100
0.67	1:25	0.307	9.23	0.289	9.29	9.26	1080
1.10	1:25	0.295	8.85	0.275	8.85	8.85	1130
1.12	1:25	0.288	8.65	0.272	8.75	8.70	1150
1.38	1:25	0.283	8.49	0.267	8.61	8.55	1170
1.38	1:25	0.281	8.45	0.264	8.49	8.47	1180
1.77	1:25	0.272	8.14	0.251	8.10	8.12	1230
2.00	1:25	0.264	7.96	0.250	8.04	8.00	1250
2.03	1:25	0.262	7.84	0.245	7.90	7.87	1270
2.18	1:25	0.258	7.75	0.241	7.75	7.75	1290
2.47	1:25	0.254	7.65	0.236	7.60	7.63	1310
2.47	1:25	0.252	7.55	0.236	7.60	7.58	1320
2.47	1:25	0.250	7.51	0.233	7.51	7.51	1330
2.62	1:25	0.249	7.47	0.231	7.45	7.46	1340
2.67	1:25	0.249	7.47	0.231	7.45	7.46	1340
2.93	1:25	0.243	7.30	0.227	7.30	7.30	1370
2.95	1:25	0.243	7.30	0.227	7.30	7.30	1370
3.18	1:25	0.236	7.08	0.217	7.00	7.04	1420

$k_f = 126 \pm 6$ liters/mol hour (from figure VI)

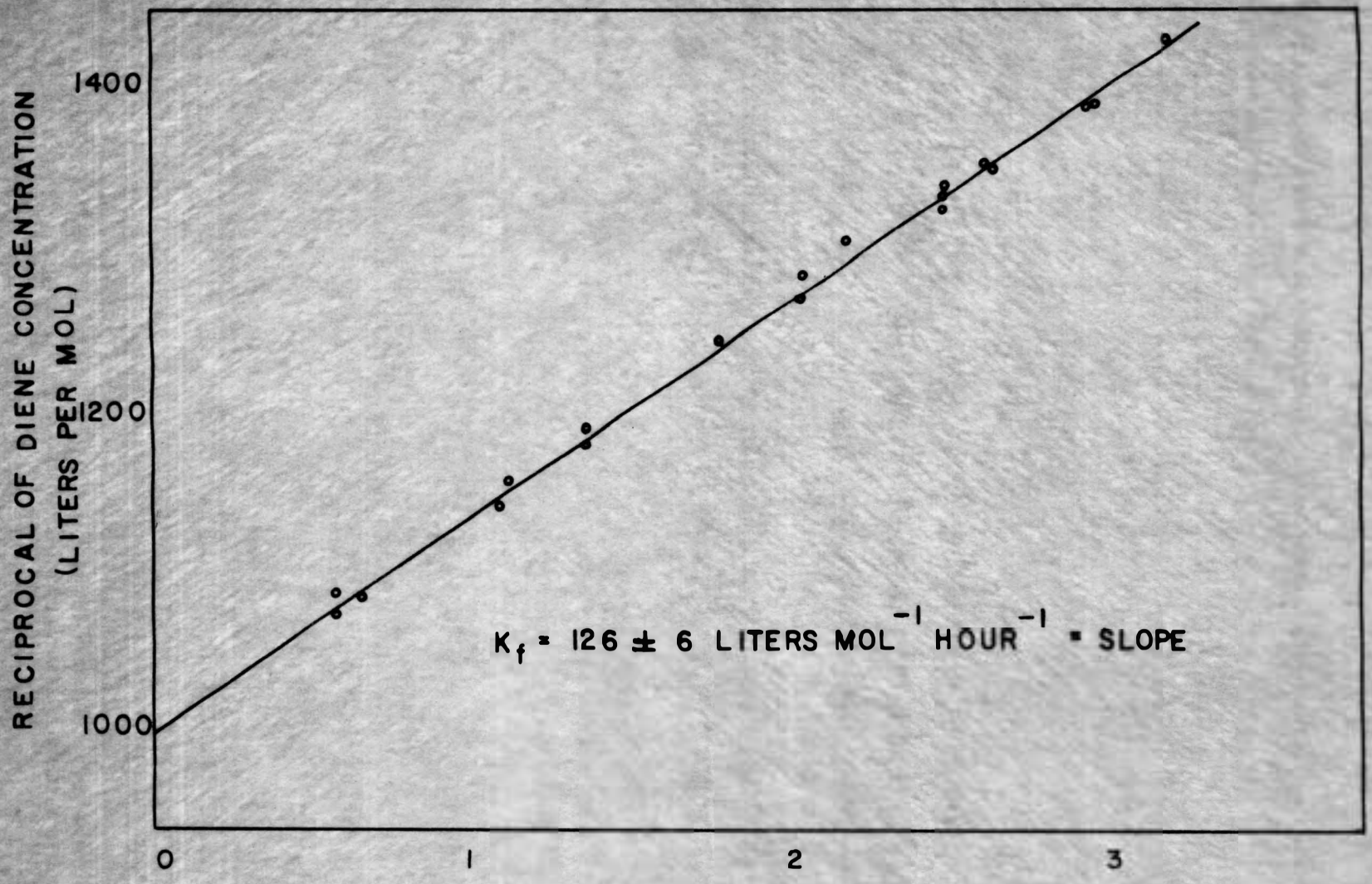

FIGURE VI DETERMINATION OF K_f AT 140° C.

Table 10. Effect of Temperature on the Forward Reaction Rate Constant

Temperature degree Kelvin	$1/T \times 10^3$ deg^{-1}	k_f 1/mol hour	log k_f
373	2.68	54.2 ± 3.2	1.73
383	2.61	67.6 ± 2.2	1.83
393	2.54	85.0 ± 2.7	1.93
413	2.42	126 ± 6.0	2.10

ΔE_a = 6.45 ± 0.61 kcal/mol (from slope, figure VII)

ΔS_f^{o*} = -.517 ± 9.4 entropy units (from intercept, figure VII)

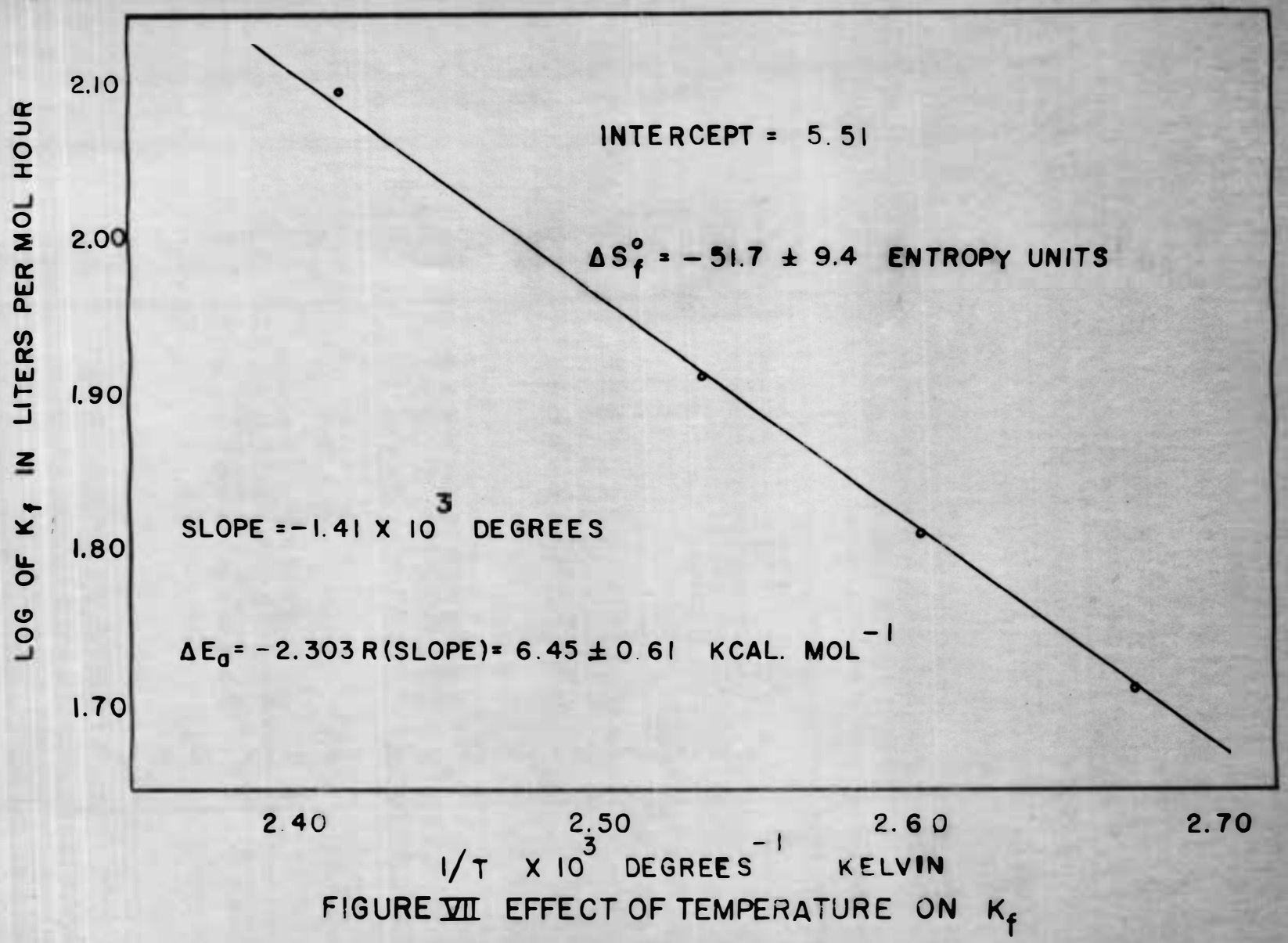

FIGURE VII EFFECT OF TEMPERATURE ON K_f

Table 11. Determination of k_f at 140° C. at a higher Concentration of Diene and Dienophile

Time hour	Dilution factor	Absorbancy at 359 mu	Diene concn, X 10^3 mols/l	Absorbancy at 378 mu	Diene concn, X 10^3 mols/l	Avg. Diene concn, X 10^3 mols/l	Reciprocal diene concn. 1/mol
0.00							500
0.25	1:50	0.300	1.80	0.280	1.80	1.80	555
0.25	1:50	0.305	1.83	0.281	1.81	1.82	548
0.50	1:50	0.278	1.67	0.258	1.66	1.67	600
0.50	1:50	0.275	1.65	0.256	1.65	1.65	605
0.75	1:50	0.258	1.55	0.247	1.53	1.54	650
0.75	1:50	0.257	1.54	0.237	1.53	1.54	650
1.00	1:50	0.233	1.40	0.220	1.42	1.41	710
1.00	1:50	0.237	1.42	0.220	1.42	1.42	704
1.25	1:50	0.218	1.31	0.203	1.31	1.31	766
1.25	1:50	0.220	1.32	0.203	1.31	1.32	759
1.50	1:50	0.203	1.22	0.188	1.21	1.22	821
1.50	1:50	0.208	1.25	0.186	1.20	1.23	810
2.00	1:50	0.183	1.10	0.169	1.09	1.10	906
2.00	1:50	0.180	1.08	0.169	1.09	1.09	920

k_f = 209 ± 12 liter/mol hour (from figure VIII)

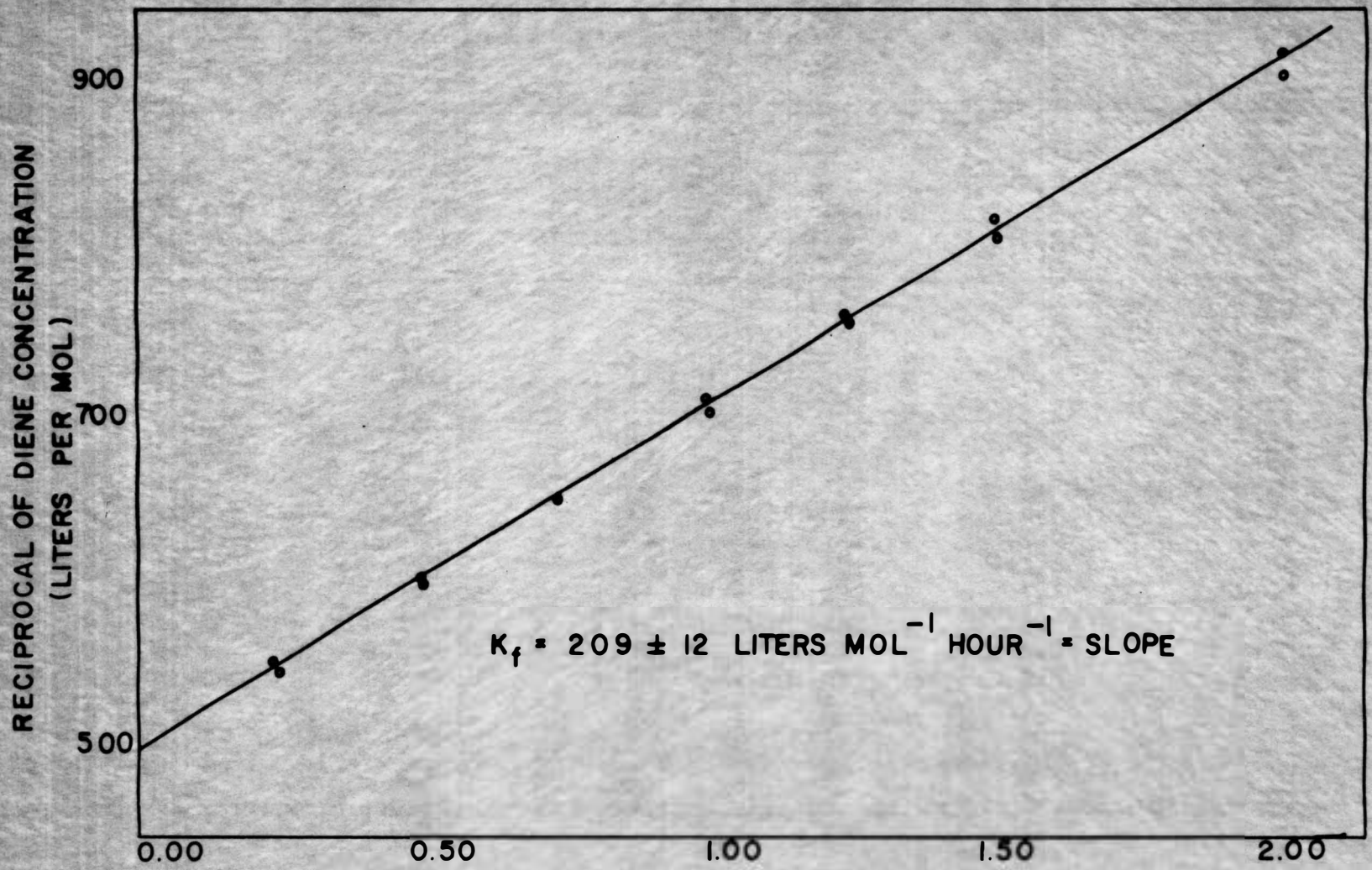

FIGURE VIII DETERMINATION OF K_f AT 140° C. USING 4×10^{-3} M DIENE AND DIENOPHILE

Table 12. Change in Concentration of Anthracene at 140° C. with an Excess of Diene

Time hour	Dilution factor	Absorbancy at 359 mu	Diene concn. X 10^3 mols/l	Absorbancy at 378 mu	Diene concn. X 10^3 mols/l	Avg. Diene conc. X 10^3 mols/l
0.00						2.00
0.25	1:50	0.315	1.89	0.296	1.91	1.90
0.25	1:50	0.318	1.91	0.300	1.93	1.92
0.50	1:50	0.308	1.85	0.287	1.85	1.85
0.50	1:50	0.308	1.85	0.287	1.85	1.85
0.75	1:50	0.302	1.82	0.279	1.80	1.81
0.75	1:50	0.293	1.76	0.279	1.80	1.78
1.00	1:50	0.283	1.70	0.272	1.75	1.73
1.00	1:50	0.288	1.73	0.269	1.73	1.73
1.50	1:50	0.275	1.65	0.248	1.60	1.63
1.50	1:50	0.275	1.65	0.248	1.60	1.63
1.75	1:50	0.262	1.57	0.250	1.61	1.59
2.00	1:50	0.257	1.54	0.242	1.56	1.55
2.00	1:50	0.258	1.55	0.241	1.55	1.55

Concentrations of anthracene = 2.00×10^{-3} mols/liter
Concentrations of maleic anhydride = 1.00×10^{-3} mols/liter

Table 13. Determination of k_f at 140° C. Using an Excess of Diene

$C_a = 2.00 \times 10^{-3}$ M. anthracene
$C_b = 1.00 \times 10^{-3}$ M maleic anhydride

Time hour	Avg. Diene* concn. $\times 10^3$ mols/l	x $\times 10^3$ mols/l	$C_a - x$ $\times 10^3$ mols/l	$C_b - x$ $\times 10^3$ mols/l	$\frac{C_a - x}{C_b - x}$	$\log \frac{C_a - x}{C_b - x}$
0.25	1.90	0.10	1.90	0.90	2.09	0.320
0.25	1.92	0.08	1.92	0.92	2.08	0.318
0.50	1.85	0.15	1.85	0.85	2.18	0.339
0.50	1.85	0.15	1.85	0.85	2.18	0.339
0.75	1.81	0.19	1.81	0.81	2.24	0.350
0.75	1.78	0.22	1.78	0.78	2.28	0.358
1.00	1.73	0.27	1.73	0.73	2.38	0.377
1.00	1.73	0.27	1.73	0.73	2.38	0.377
1.50	1.63	0.37	1.63	0.63	2.59	0.413
1.50	1.63	0.37	1.63	0.63	2.59	0.413
1.75	1.59	0.41	1.59	0.59	2.70	0.431
2.00	1.55	0.45	1.55	0.55	2.83	0.452
2.00	1.55	0.45	1.55	0.55	2.81	0.450

$k_f = 170 \pm 10$ liters/mol hour (from figure IX)

*Table 12

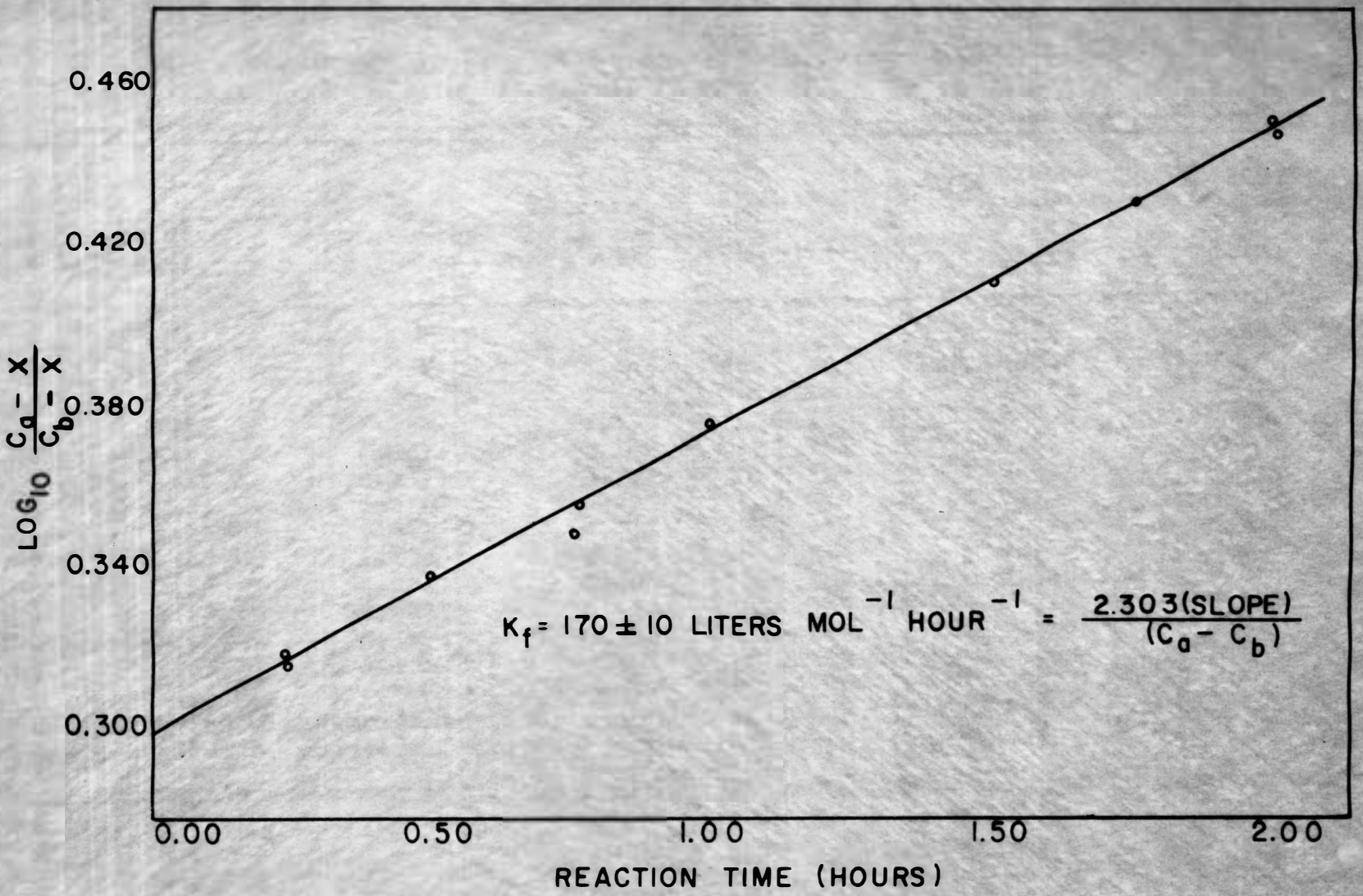

FIGURE IX DETERMINATION OF K_f AT 140° C.
USING AN EXCESS OF DIENE

Table 14. Change in Concentration of Anthracene at 140° C. with an Excess of Dienophile

Time hour	Dilution factor	Absorbancy at 359 mu	Diene concn, X 10^3 mols/l	Absorbancy at 378 mu	Diene concn. X 10^3 mols/l	Avg. Diene concn, X 10^3 mols/l
0.00						1.00
0.25	1:25	0.302	0.905	0.282	0.907	0.906
0.25	1:25	0.307	0.920	0.284	0.915	0.918
0.50	1:25	0.278	0.835	0.259	0.835	0.835
0.50	1:25	0.281	0.842	0.261	0.841	0.842
0.75	1:25	0.257	0.772	0.239	0.771	0.772
0.75	1:25	0.256	0.771	0.240	0.772	0.772
1.00	1:25	0.237	0.711	0.223	0.719	0.715
1.00	1:25	0.238	0.714	0.220	0.710	0.712
1.50	1:25	0.202	0.608	0.189	0.609	0.609
1.50	1:25	0.204	0.610	0.192	0.615	0.613
2.00	1:25	0.177	0.529	0.165	0.529	0.529
2.00	1:25	0.178	0.535	0.164	0.527	0.531

Concentration of anthracene = 1.00×10^{-3} mols/liter
Concentration of maleic anhydride = 2.00×10^{-3} mols/liter

Table 15. Determination of k_f at 140° C. Using an Excess of Dienophile

$C_a = 2.00 \times 10^{-3}$ M maleic anhydride
$C_b = 1.00 \times 10^{-3}$ M anthracene

Time hour	Avg. Diene* concn. $\times 10^3$ mols/l	x $\times 10^3$ mols/l	$C_a - x$ $\times 10^3$ mols/l	$C_b - x$ $\times 10^3$ mols/l	$\frac{C_a - x}{C_b - x}$	$\log \frac{C_a - x}{C_b - x}$
0.25	0.906	0.09	1.91	0.91	2.10	0.322
0.25	0.918	0.08	1.92	0.92	2.09	0.320
0.50	0.835	0.16	1.84	0.84	2.20	0.342
0.50	0.842	0.16	1.84	0.84	2.19	0.340
0.75	0.772	0.23	1.77	0.77	2.30	0.362
0.75	0.772	0.23	1.77	0.77	2.30	0.362
1.00	0.715	0.28	1.72	0.72	2.40	0.380
1.00	0.712	0.29	1.71	0.71	2.41	0.382
1.50	0.609	0.39	1.61	0.61	2.64	0.422
1.50	0.613	0.39	1.61	0.61	2.64	0.422
2.00	0.529	0.47	1.53	0.53	2.89	0.461
2.00	0.531	0.47	1.53	0.53	2.89	0.461

$k_f = 184 \pm 8$ liters/mol hour (from figure X)

* from Table 14

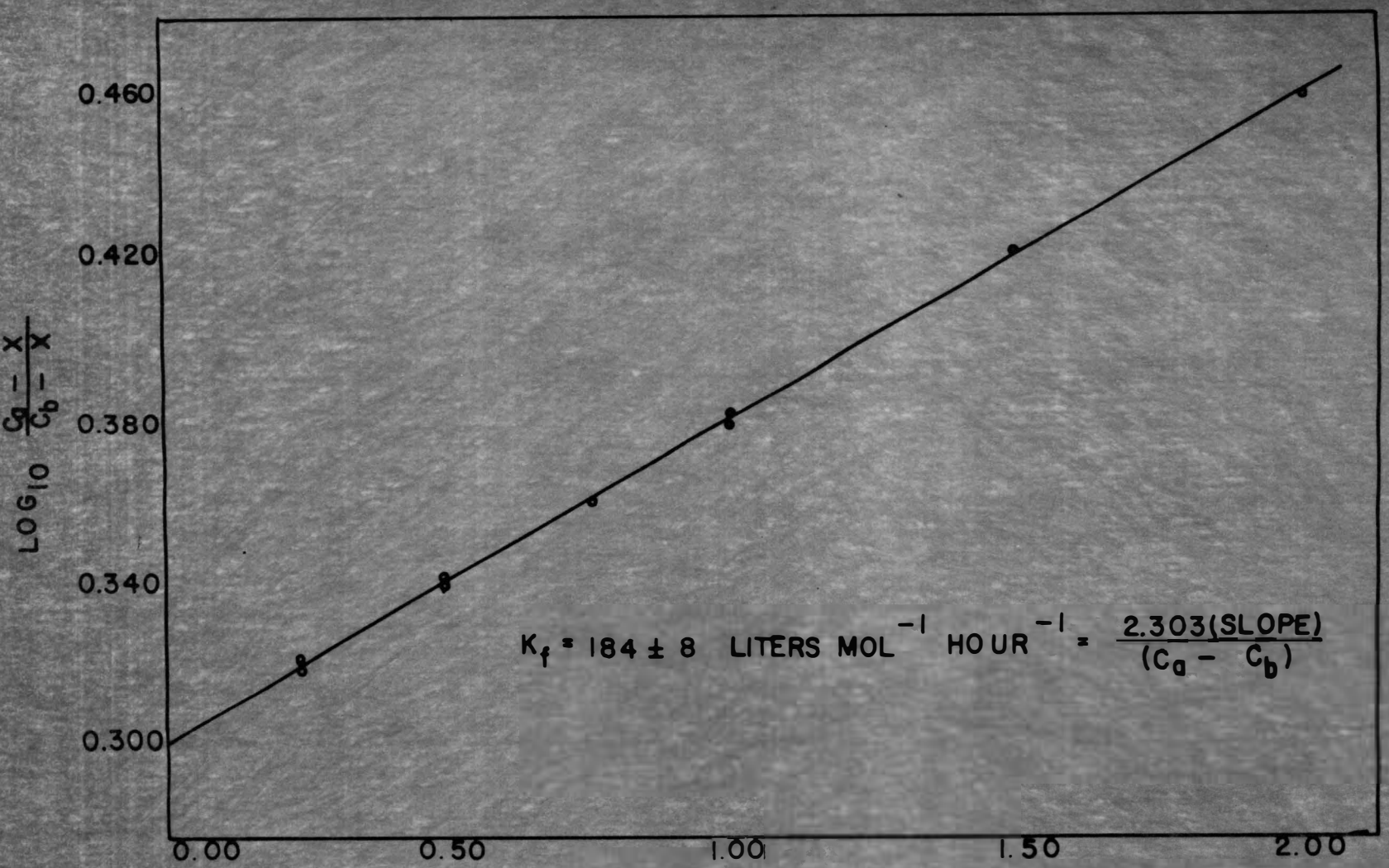

FIGURE X DETERMINATION OF K_f AT 140° C.
USING AN EXCESS OF DIENOPHILE

Table 16. Determination of k_r at 100° C.

Time hour	Absorbancy at 359 mu	Diene concn. X 10^6 mols/l	Absorbancy at 378 mu	Diene concn. X 10^6 mols/l	Avg. Diene concn. X 10^6 mols/l	Adduct concn. X 10^3 mols/l	Log Adduct concn.
18.00	0.029	3.44	0.026	3.40	3.42	1.9966	-2.6997
18.00	0.028	3.37	0.027	3.41	3.39	1.9966	-2.6997
24.00	0.032	3.85	0.030	3.90	3.88	1.9961	-2.6998
24.60	0.039	4.59	0.037	4.71	4.70	1.9953	-2.7000
36.00	0.041	4.89	0.038	4.89	4.89	1.9951	-2.7003
36.00	0.042	4.95	0.040	4.90	4.93	1.9951	-2.7003
48.00	0.043	5.12	0.041	5.10	5.11	1.9949	-2.7007
48.00	0.070	8.36	0.065	8.38	8.37	1.9916	-2.7008
61.20	0.086	10.3	0.081	10.5	10.4	1.9896	-2.7012
61.20	0.088	10.6	0.084	10.8	10.7	1.9893	-2.7013
72.00	0.100	12.0	0.093	12.0	12.0	1.9880	-2.7016
72.00	0.102	12.3	0.099	12.5	12.5	1.9875	-2.7017

$k_r = 2.76 \pm 0.06 \times 10^{-5}$ hour^{-1} (from figure XI)

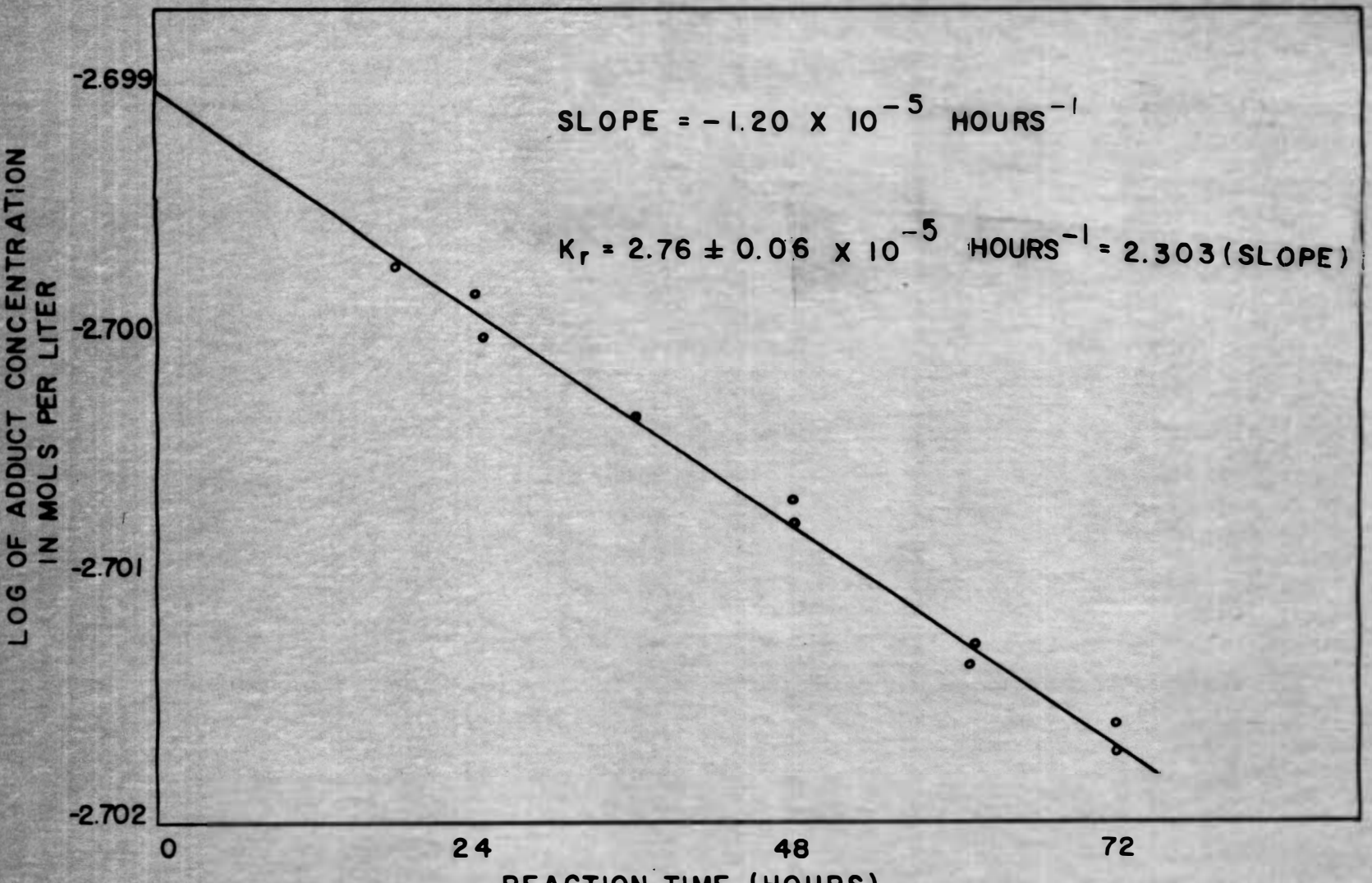

FIGURE XI DETERMINATION OF K_r AT 100° C.

Table 17. Determination of k_r at 110° C.

Time hour	Absorbancy at 359 mu	Diene concn. X 10^6 mols/l	Absorbancy at 378 mu	Diene concn. X 10^6 mols/l	Avg. Diene concn. X 10^6 mols/l	Adduct concn. X 10^3 mols/l	Log adduct concn.
18.00	0.025	2.95	0.023	2.90	2.93	1.9971	-2.6996
18.00	0.028	3.40	0.026	3.35	3.37	1.9966	-2.6997
24.60	0.039	4.70	0.037	4.72	4.71	1.9953	-2.7000
25.20	0.036	4.34	0.033	4.26	4.30	1.9957	-2.6999
36.00	0.051	6.17	0.047	6.11	6.14	1.9939	-2.7003
36.00	0.055	6.60	0.051	6.55	6.58	1.9934	-2.7004
48.00	0.067	8.03	0.062	7.99	8.01	1.9920	-2.7007
48.00	0.071	8.45	0.065	8.40	8.43	1.9916	-2.7008
60.60	0.090	10.8	0.082	10.6	10.7	1.9893	-2.7013
72.00	0.106	12.7	0.095	12.3	12.5	1.9875	-2.7017
72.00	0.108	13.0	0.100	12.9	13.0	1.9870	-2.7018

$k_r = 8.91 \pm 0.10 \times 10^{-5}$ hour^{-1} (from figure XII)

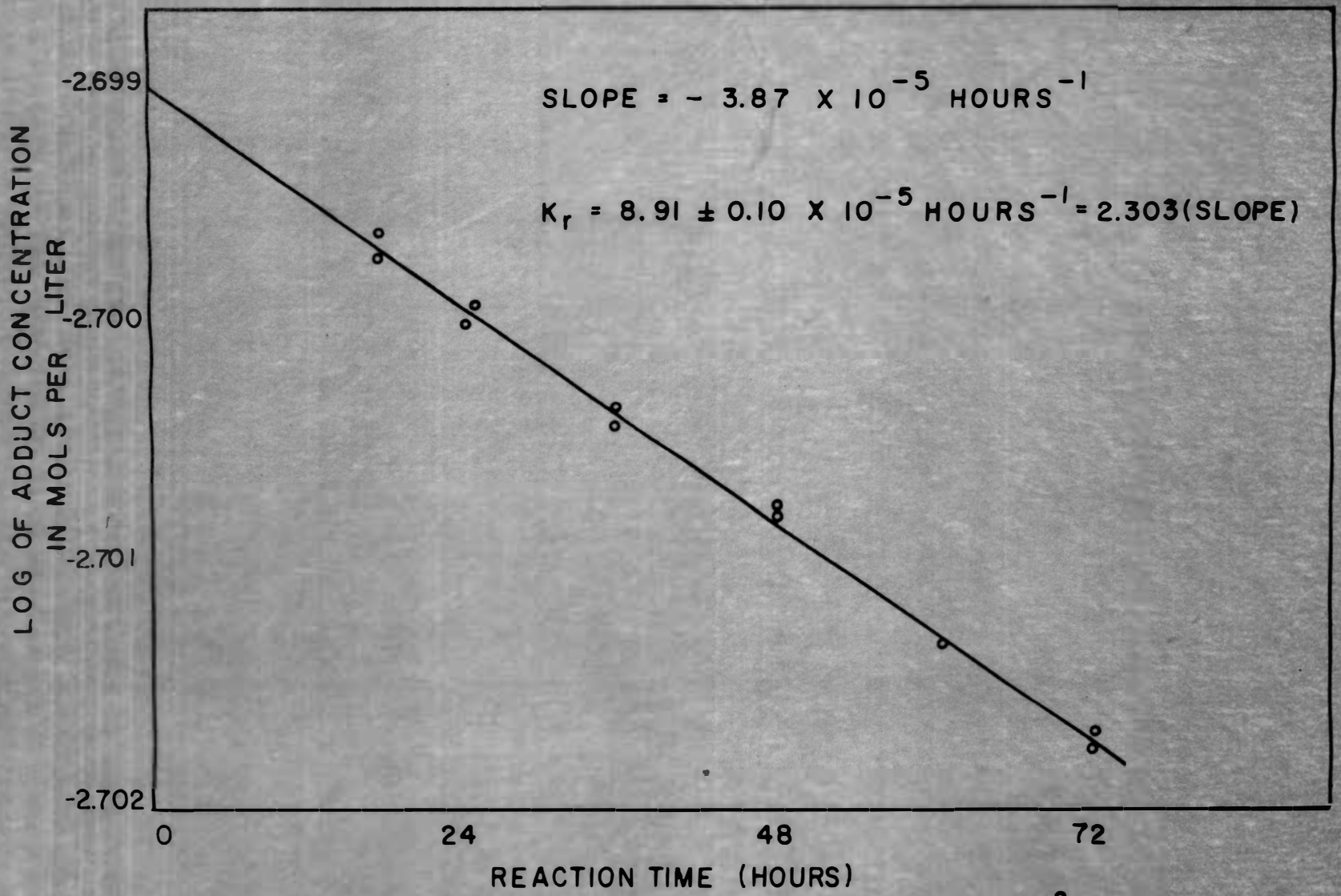

FIGURE XII DETERMINATION OF K_r AT 110° C.

Table 18. Determination of k_r at 120° C.

Time hour	Absorbancy at 359 mu	Diene concn. X 10^6 mols/l	Absorbancy at 378 mu	Diene concn. X 10^6 mols/l	Avg. Diene concn. X 10^3 mols/l	Adduct concn. X 10^3 mols/l	Log adduct concn.
2.57	0.012	1.44	0.011	1.42	1.43	1.9986	-2.6993
2.57	0.012	1.44	0.011	1.42	1.43	1.9986	-2.6993
3.97	0.018	2.16	0.017	2.24	2.20	1.9978	-2.6995
4.27	0.022	2.64	0.020	2.60	2.62	1.9974	-2.6995
12.40	0.068	8.16	0.062	8.20	8.18	1.9918	-2.7008
12.40	0.062	7.44	0.060	7.70	7.57	1.9924	-2.7006
19.40	0.104	12.4	0.097	12.5	12.5	1.9875	-2.7017
19.40	0.106	12.7	0.098	12.6	12.7	1.9873	-2.7017
23.00	0.122	14.6	0.114	14.7	14.7	1.9853	-2.7022
23.00	0.125	15.0	0.116	15.0	15.0	1.9850	-2.7023

$k_r = 3.22 \pm 0.06 \times 10^{-4}$ hour^{-1} (from figure XIII)

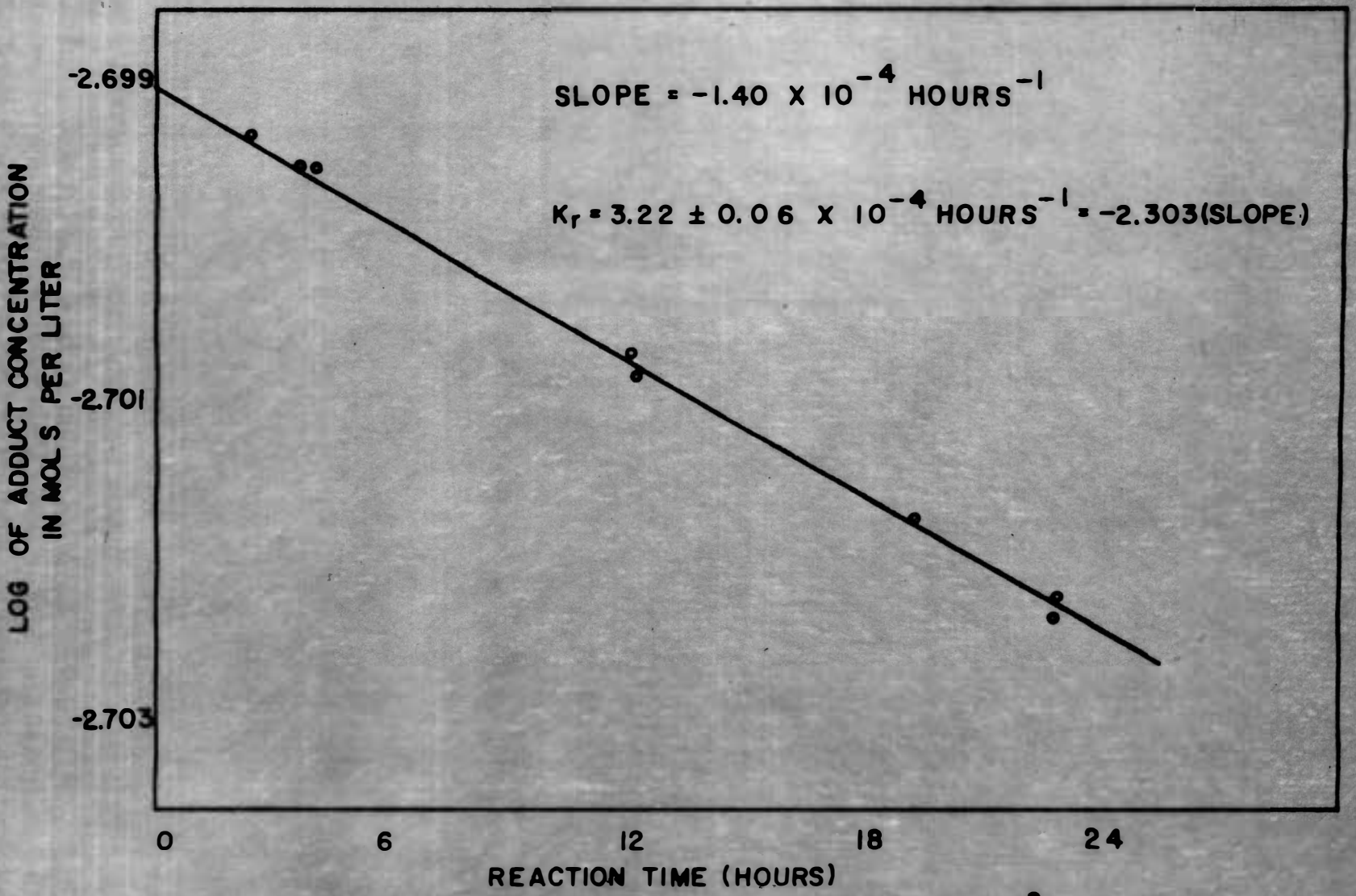

FIGURE XIII DETERMINATION OF K_r AT 120°C.

Table 19. Determination of k_r at 140° C.

Time hour	Absorbancy at 359 mu	Diene concn. X 10^5 mols/1	Absorbancy at 378 mu	Diene concn. X 10^5 mols/1	Avg. Diene concn. X 10^5 mols/1	Adduct concn. X 10^3 mols/1	Log adduct concn.
2.88	0.175	2.10	0.159	2.05	2.08	1.9792	-2.7035
2.88	0.162	1.94	0.150	1.93	1.94	1.9806	-2.7032
5.00	0.297	3.56	0.278	3.58	3.57	1.9643	-2.7068
5.00	0.291	3.49	0.263	3.39	3.44	1.9656	-2.7065
8.00	0.425	5.70	0.446	5.75	5.73	1.9427	-2.7116
8.20	0.458	5.50	0.431	5.55	5.53	1.9445	-2.7112
12.00	0.619	7.43	0.572	7.37	7.40	1.9260	-2.7176
12.10	0.687	8.25	0.644	8.30	8.27	1.9173	-2.7173
16.00	0.916	11.0	0.838	10.8	10.9	1.8910	-2.7233
20.00*	0.113	13.6	0.105	13.5	13.6	1.8638	-2.7296
20.00*	0.114	13.7	0.106	13.6	13.7	1.8630	-2.7298

*these samples were diluted 1:10 before analysis

$k_r = 3.54 \pm 0.13 \times 10^{-3}$ hour^{-1} (from figure XIV)

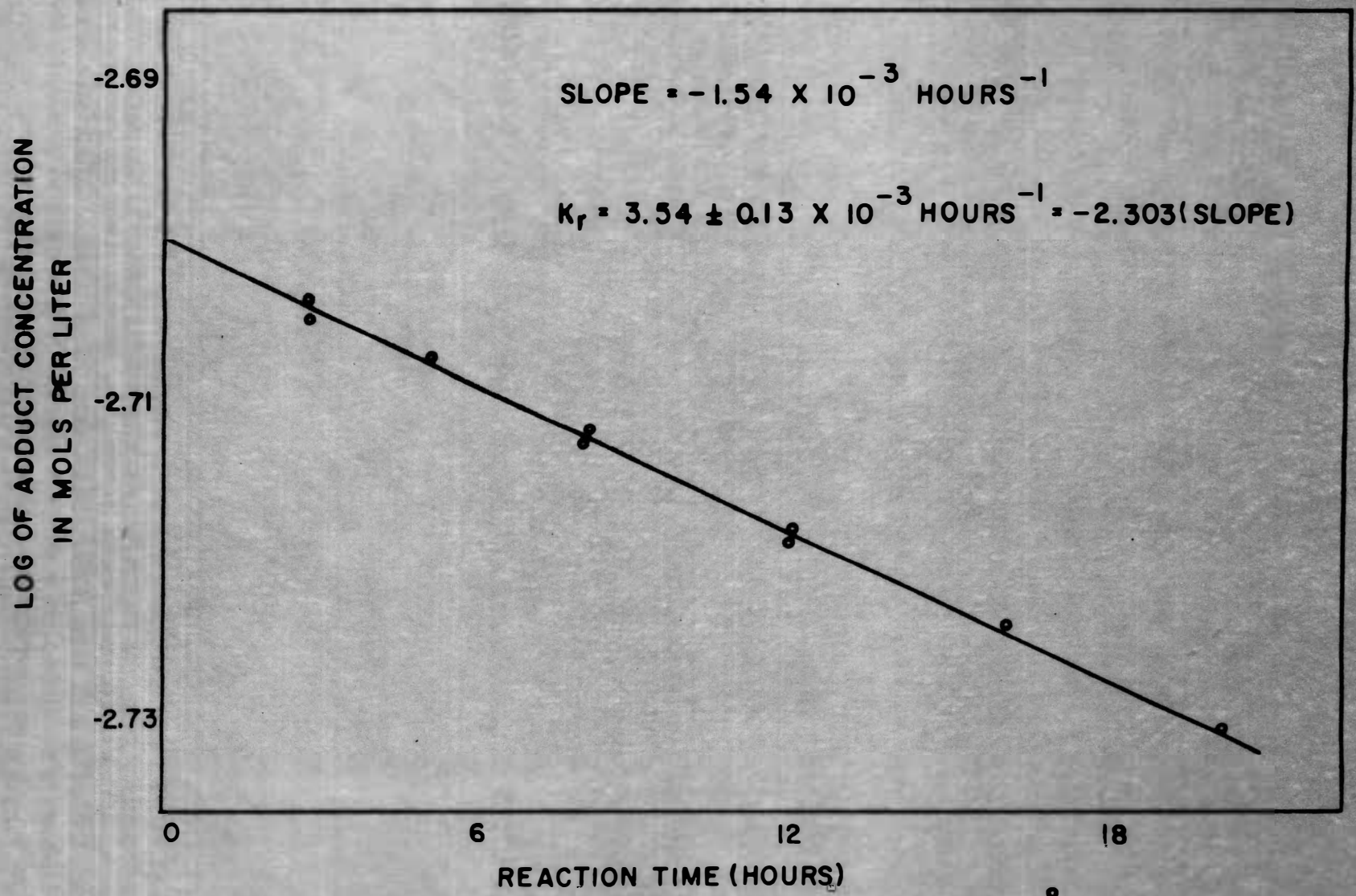

FIGURE XIV DETERMINATION OF K_r AT 140°C.

Table 20. Determination of the Order of the Reverse Reaction

	Temperature 120° C.	140° C.
Equilibrium constant (calculated from the equilibrium composition)	2.63×10^5	0.918×10^5
Equilibrium constant calculated on the supposition that the reverse reaction is zero order	1310×10^5	146×10^5
Equilibrium constant calculated on the supposition that the reaction is first order*	2.64×10^5	0.354×10^5
Equilibrium constant calculated on the supposition that the reverse reaction is second order	0.0525×10^5	0.00588×10^5

*Agreement of these values with the values known from the equilibrium composition establishes the reverse reaction as of the first order.

Table 21. Effect of Temperature on the Reverse Reaction Rate Constant

Temperature degree Kelvin	$1/T \times 10^3$ deg^{-1}	$k_r \times 10^4$ $hour^{-1}$	log k_r
373	2.68	0.276 ± 0.006	-4.56
383	2.61	0.891 ± 0.010	-4.05
393	2.54	3.22 ± 0.06	-3.49
413	2.42	35.5 ± 1.3	-2.45

ΔE_a = 35.0 ± 4.6 kcal/mol (from slope, figure XV)

ΔS_f^{o*} = 3.0 ± 0.1 entropy units (from intercept, figure XV)

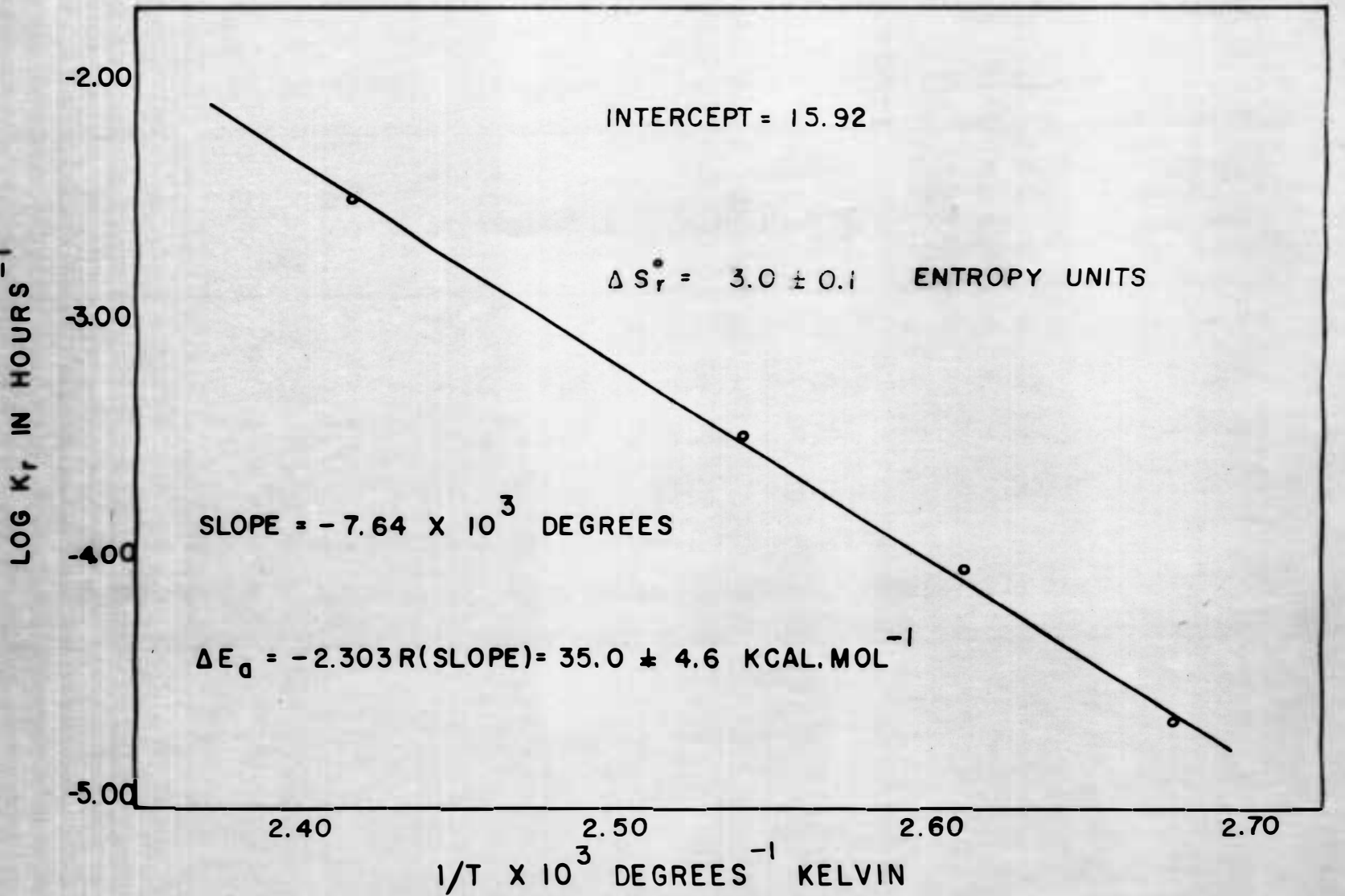

FIGURE XV EFFECT OF TEMPERATURE ON K_r

Table 22. Effect of Temperature on the Equilibrium Constant

Temperature degree Kelvin	$1/T \times 10^3$ deg^{-1}	k_f from Figs.III-VII 1/mol hour	$k_r \times 10^4$ from Figs.XI-XIV $hour^{-1}$	$K \times 10^{-5}$ calculated as (k_f/k_r)	log K calcd. from previous column
373	2.68	54.2 ± 3.2	0.276 ± 0.006	19.6	6.29
383	2.61	67.6 ± 2.2	0.891 ± 0.010	7.59	5.88
393	2.54	85.0 ± 2.7	3.22 ± 0.06	2.64	5.42
413	2.42	126 ± 6	35.5 ± 1.3	0.354	4.55

ΔE_a = -25.9 ± 4.1 kcal/mol (from slope, figure XVI)

ΔS^o = -40.8 ± 6.5 entropy units (from intercept, figure XVI)

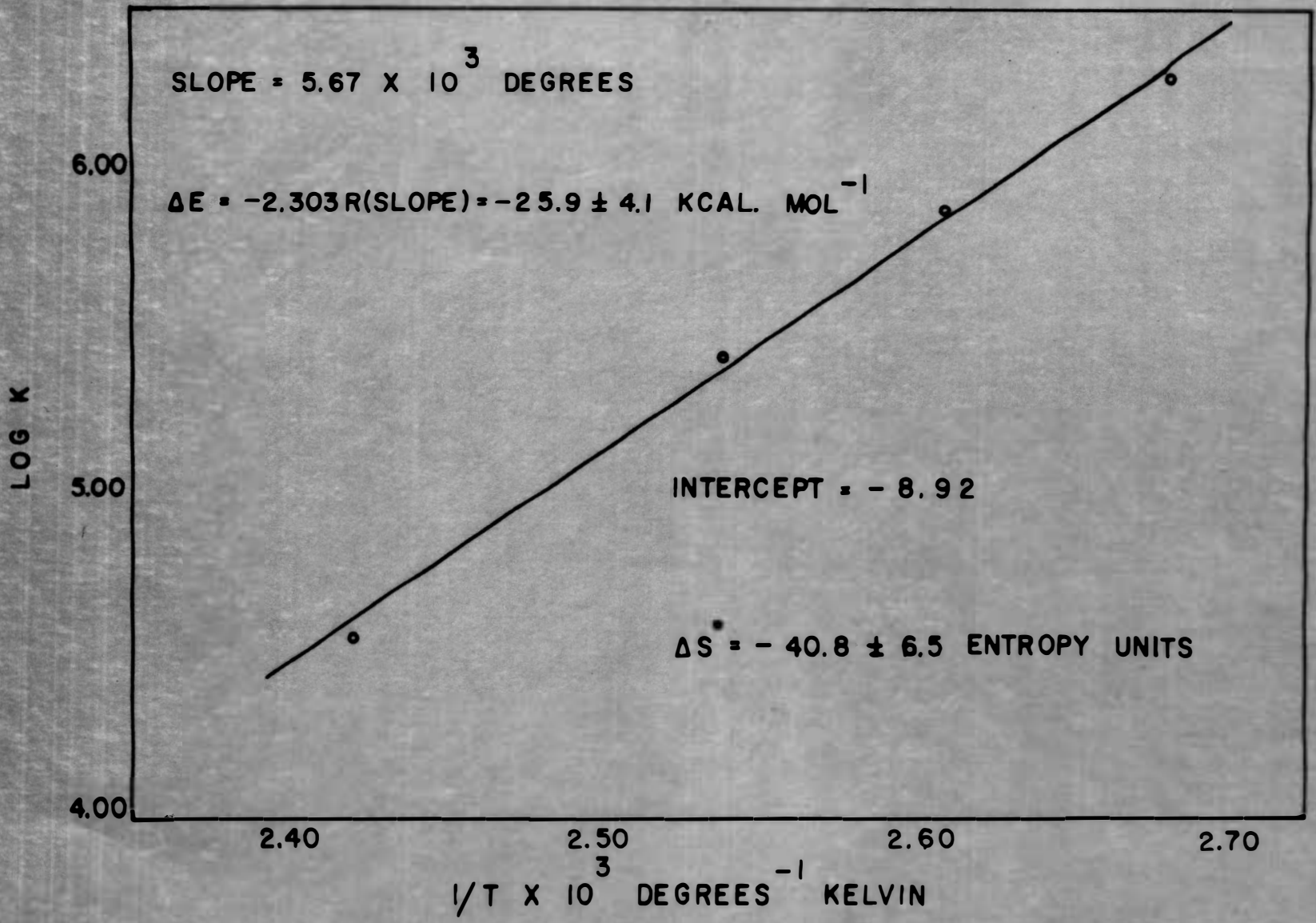

FIGURE XVI EFFECT OF TEMPERATURE ON K

Table 23. Free Energy Changes for the Reaction

Temperature degree Kelvin	ΔF^{o} kcal/mol		
	Forward reaction	Reverse reaction	Complete reaction
373	18.8 ± 1.4	29.8 ± 0.6	-10.6 ± 0.7
383	19.1 ± 0.6	29.7 ± 0.4	-10.2 ± 0.3
393	19.4 ± 0.6	29.5 ± 0.6	- 9.8 ± 0.3
413	20.1 ± 1.0	29.3 ± 1.0	- 9.1 ± 0.4

DISCUSSION OF RESULTS

In order to conduct a kinetic study of a chemical reaction, it is necessary to determine the change in concentration of one of the reactants as a function of time. Most often this change in concentration may be observed by noting a change in a particular physical property of this reactant. Inspection of the ultraviolet absorption spectrum of anthracene with maxima at 326, 352, 359, and 378 millimicrons illustrates the feasibility of utilizing this physical property to conduct a kinetic study of a reaction involving anthracene in view of the transparent nature of maleic anhydride and the adduct.

In order to obtain valid kinetic data, the various compounds used in the study were purified by methods described earlier. Maleic anhydride with a melting point of 51° C. was analyzed by the non-aqueous titration method of Huhn and Jenckel (44). By this analysis the anhydride samples were found to contain an average value of 98.3% maleic anhydride and 1.7% maleic acid. Since the acid and anhydride have similar molecular weights, 116.07 and 98.06 respectively, the resulting concentration errors of four parts per thousand are of little consequence compared to other experimental errors. However, had the maleic anhydride contained 1.7% inert material instead of acid, the errors would be much larger.

The blue-violet, fluorescent anthracene melted sharply at 216° C. while the adduct, which was prepared by the method of Bachmann and Kloetzel (2) melted at 264° C. to form a colorless liquid. The adduct was also analyzed for carbon and hydrogen. $C_{18}H_{12}O_3$ requires 78.25% C, 4.38% H, and 17.37% O. Duplicate analyses yielded 78.38% C, 4.49% H, and 17.13% O; thus giving experimental evidence on the adduct purity. Furthermore, a xylene solution of the adduct investigated spectrophotometrically did not exhibit an absorbancy at the anthracene absorbancy maxima, hence the adduct was not contaminated with unreacted anthracene. These observations agree with the carbon and hydrogen analysis for the adduct.

It was discovered that the concentration of anthracene at 359 and 378 millimicrons changed appreciably in xylene solutions containing oxygen indicating the instability of anthracene in the solvent. This was true when either the xylene solution was exposed to light or kept in the dark, except that the change was of a greater magnitude when the solution was exposed to a light source. It was also found that when boiled xylene was used as the solvent for anthracene and stored in the dark, only a very slight concentration change could be detected spectrophotometrically at 359 and 378 millimicrons over a period of 100 hours. All of the changes resulted in an increase in the anthracene concentration as indicated in Tables 3 and 4. This change in

anthracene concentration could be perhaps due to a compound or several compounds being formed in some manner that have high molar absorbancy indexes at or near 359 and 378 millimicrons. Anthraquinone, alizarin, and quinizarin could be some of the possibilities. Studies are not available that report spectra of these compounds under the desired experimental conditions; however, the spectra of anthraquinone in ether has been reported and the results agree with the above postulates.

Difficulty in obtaining reproducible results for a Beer's law curve of anthracene in xylene at 25° C. was also experienced. It was discovered that commercial xylene containing dissolved oxygen could not be used as a solvent because the anthracene would undergo reactions of perhaps a photochemical nature. Since under these conditions the data would not conform to Beer's law, certain precautions had to be employed. It was decided that perhaps an inert gas could be bubbled through the xylene to displace any dissolved oxygen. Nitrogen was the first gas used. After several Beer's law curves for anthracene had again been determined using the nitrogen, erratic results were still being obtained, although the molar absorbancy indexes of anthracene at 359 and 378 millimicrons were much higher than those previously reported by either Hazlett and co-workers (41) using chloroform as a solvent or Krzyzaniak (52) using xylene as a solvent. It

was then decided that perhaps there may be a solvent interaction of some type with the nitrogen. To test this postulate, a degassed xylene solution was prepared by the conventional method of freezing and thawing the xylene under a vacuum and used as the reference standard. Spectra of oxygen, nitrogen, and helium-saturated xylene solutions were then determined. The results showed that the solutions saturated with oxygen and nitrogen exhibited appreciable absorbancies in the range of 320 to 400 millimicrons; while the xylene saturated with helium did not.

These results were surprising and had not previously been reported. However, Tsubomura and Mulliken (72) later reported results of a similar nature indicating that a charge-transfer complex is formed between various solvents and oxygen. The same conclusions can be made from the results obtained in this study.

In view of the above experiments, it was necessary to use helium-saturated boiled xylene, shown to have the same optical properties as the xylene prepared by freezing and thawing, in all further experiments. The helium was also used in an attempt to keep the oxygen content of the xylene solutions at a minimum as it had been reported that as few as several parts per million of oxygen will catalyze the photochemical oxidation of anthracene to its photo-oxide (58).

Beer's law curves of anthracene in the above described solvent system were then obtained and the results were reproducible. The molar absorbancy indexes, however, were still higher at the two maxima than the values reported by previous workers. This demonstrates that the anthracene used in this study is of a higher purity than that used by either Krzyzaniak or Hazlett; although the absorption maxima are the same in all three studies, that is, 326, 342, 359, and 378 millimicrons.

In order to simplify the mathematical treatment, it was desirable to use equimolar concentrations of reactants initially. For the forward reaction, equal volumes of anthracene and maleic anhydride were used and placed in ampoules by means of calibrated pipettes using quantitative procedures. Exact volume measurements were unnecessary in the reverse reaction. Hence, this procedure introduces a volume error which is present in the forward reaction, but not in the reverse. Additional errors are also introduced when the solutions to be analyzed are diluted to the range in which Beer's law is valid.

In rate determinations of the forward reactions, it was necessary to use fresh solutions of anthracene for each determination as it was discovered that the rate constants would decrease if the same solution were used 48 hours later, in spite of the fact that the solution was stored in the dark in an atmosphere of helium. The forward reaction rate constant

at 100° C. decreased from a value of 54.2 to 38.3 liters per mol/hour when again determined 48 hours later, in using the same initial anthracene solution. The necessity of preparing these fresh anthracene solutions before such determination introduces errors due to weight and temperature effects.

To check the precision of the experimental results, k_f was determined in duplicate at 120° C. using a second freshly prepared anthracene solution. The forward reaction rate constant obtained, 87.5 liters per mol hour, compares favorably with the value of 85.0 liters per mol hour that is being used as the value in this study. The reproducibility of the results cannot always guarantee the accuracy of the rate measurement, since the determinations may involve a constant source of error, e.g., presence of an impurity.

In order to displace the air, the ampoules were filled with helium prior to filling them with the reaction mixtures. This was performed so that the anthracene would undergo only one reaction, the reaction with maleic anhydride. This precaution proved beneficial because it was demonstrated that ampoules containing only anthracene in xylene and filled with helium did not suffer a change in anthracene concentration as a function of time. This clearly demonstrated that the oxygen present in the air had been effectively displaced from the reaction system.

The forward reaction was established as of the second-order by the proportionality of the reciprocal of the diene concentration as a function of time. When higher equimolar concentrations of diene and dienophile were used, i.e., 4.00×10^{-3} moles/liter at 140° C., second-order kinetics were also obeyed. This indicates that the forward reaction is second-order in a limited range of concentration. Other workers (52,74) studying the same reaction, while not exercising the same precautions, have found that the forward reaction between anthracene and maleic anhydride obeys the second-order rate law up to an initial equimolar concentration ratio of diene and dienophile of 0.02 moles per liter. The second-order rate law does not necessarily have to be obeyed at either higher or lower concentrations however. It has been reported that some gas reactions obey several rate laws depending upon the partial pressure of the gas.

In a separate series of experiments at 140° C., unequal concentrations of diene and dienophile were employed. Using an excess of diene, i.e., 4.00×10^{-3} moles/liter and 2.00×10^{-3} moles/liter dienophile, results were obtained that indicated that the reaction is of the second-order. The reaction was also found to be second-order when an excess of dienophile was used, i.e., 4.00×10^{-2} moles/liter, and 2.00×10^{-3} moles/liter diene. Hence, the forward reaction is bimolecular and second-order with respect to both the anthracene and the maleic

anhydride in the concentration range studied. It would be highly optimistic to state that the forward reaction is bimolecular in all cases since only a limited concentration range was studied. In order to be able to state explicitly that the reaction is absolutely bimolecular, a wide range of concentrations in which the concentration of both the diene and dienophile were varied should be studied.

One thing that should be noted is the fact that all spectrophotometric readings for both the forward and reverse reactions were read at a constant temperature of 25° C. This temperature was maintained through the use of a centrifugal pump that circulated water continuously through the spectrophotometer cell and lamp housing compartments from a constant temperature bath maintained at the desired temperature, 25° C. This precaution was necessary since Tunnicliff and coworkers (73) have reported that the absorbancy of butadiene changed by as much as 0.5% with just a change of one degree in the temperature.

The entropy of activation for the forward reaction as determined from the intercept of the curve in Figure VII was found to be -51.7 entropy units. Since entropy, using a qualitative approach, is a measure of the order or disorder of the system under consideration, a decrease in entropy, which is indicated by a negative sign, would signify that the system is becoming more ordered. If there is a complex being formed,

it has a much more ordered configuration when compared to the order of the initial state of the system, i.e., the anthracene and the maleic anhydride molecules in xylene solution, which should be under normal conditions a completely random disorderly system.

In the determination of the reverse reaction, it was also necessary to prepare fresh solutions before each kinetic experiment. The errors here would also be the same as those experienced in the forward reaction. The necessity of preparing these fresh solutions is dictated by the fact that the adduct decomposes slowly even at room temperature to form anthracene and maleic anhydride.

The reverse reaction does not proceed to a sufficient extent to determine the order of the reaction from kinetic data alone. To circumvent this, equilibrium constants evaluated from equilibrium mixtures at 120 and 140° C. were used. The kinetic data for the reverse reactions at those two temperatures were then utilized and provisional equilibrium constants were calculated assuming that the reaction employed obeyed zero-, first-, and second-order kinetics. These values were then compared with the values of the equilibrium constant, as illustrated in Table 20, obtained by analyzing the reaction mixtures at equilibrium. Agreement could only be reached if the reverse reaction was assumed to be of the first-order. This agrees with other investigators in Diels-Alder reaction

research, who, in every case, determined that the reverse reaction was of order one.

It might be contended that for any given reaction the experimental data would fit a range of order-values, i.e., the data in the above cases would approximately fit all orders from perhaps 0.8 to 1.2. However, one needs to consider as plausible only orders for integral values, or, occasionally, simple fractional orders, i.e., 3/2, since the order of precision of the kinetic measurements is not sufficiently high to support these fractional orders.

Since there is an estimated error on every experimentally determined value in this study, it was not necessary to smooth values as done in previous studies (28,52).

The entropy of the over-all reaction was determined from the intercept of the curve in Figure XVI. This value is -40.8 entropy units which when compared to the entropies of activation for the forward and reverse reaction, -51.7 and 3.0 entropy units respectively, indicates that the entropy value for the over-all reaction is approximately equal to the entropy of activation for the forward reaction. This would seem to indicate that the activated complex has a configuration very similar to that of the adduct. If the results of this study can be accorded significance, the following statement will be directly applicable. "In bimolecular reactions the complex is formed by association of two individual molecules, and there is a loss of translational and rotational freedom,

so that ΔS_f^{o*} is negative. In fact, ΔS_f^{o*} is not notably different from ΔS^o for the complete reaction. This situation is often found in reactions of the type

$$A + B \dashrightarrow AB$$

and indicates that the activated complex (AB)* is similar to the product molecule AB" (60) in structure. As to the mechanism of the Diels-Alder reaction, however, the kinetic data reported here is inconclusive in the support of any of the proposed geometric configurations of the transition state.

The standard state free energy changes for the forward, reverse, and over-all reactions are summarized in Table 23. The results indicate that the over-all reaction proceeds spontaneously.

All of the estimated errors in the rate constants were calculated assuming that the spectrophotometric techniques used were without error. This statement is not entirely true, however, as the maximum precision that can be attained on most spectrophotometers is $\pm$ 1% when using ordinary methods of analysis.

The results of this study can be easily compared with those of Krzyzaniak (52) and this is illustrated in Tables 24 and 25. It should be remembered that his results were obtained without employing the precautions used in this study. Both studies do demonstrate, however, that the reaction is exothermic

and that the equilibrium constants decrease as the temperature increases. The equilibrium constants, the forward and the reverse reaction rate constants found in this study are all of a larger magnitude than those obtained by Krzyzaniak. The thermodynamic properties evaluated, however, are of the same magnitude.

Perhaps the most satisfactory explanation of the apparent disagreement of the values of the rate constants in this study and the values obtained earlier by Krzyzaniak can be based upon the formation of the triplet state of anthracene. Since, as a result of photochemical processes, the triplet state of anthracene is formed rather easily under the proper conditions, i.e., light and oxygen, the concentration of the anthracene is misrepresented as this excited state of anthracene does not absorb in the same spectral region as the unexcited anthracene molecules.

If this is the situation, the low values obtained for the various forward reaction rate constants in the kinetic study performed by Krzyzaniak are easily explained. The triplet state, by assumption, is formed immediately and then goes through a process of releasing the excited molecules at a definite rate onto the ground state. Some of the excited molecules may also react photochemically to form other compounds of an unknown nature. The maleic anhydride, under these conditions, will only be able to react with the unexcited

molecules of anthracene which are being formed at a definite rate. Therefore, the rate constants of the forward reactions are dependent upon the release of the photochemically excited anthracene molecules to the ground state and this process will not represent a true Diels-Alder kinetic study.

In the reverse reaction, a similar situation exists which yields lower values for the reverse reaction rate constants. The anthracene which is formed from the thermal dissociation of the adduct is very rapidly photochemically excited to the triplet state of anthracene. This excited species is again released at a definite rate from which the reverse reaction rate constant is being determined.

In the present study, some or all of this photochemical conversion process has been effectively eliminated as evidenced by the larger values obtained for the various rate constants.

Vaughan and Andersen (74) obtained values for the forward and reverse reaction rate constants for the reaction between anthracene and maleic anhydride in propionic acid at 142° C. Their values, 92.6 liters per mol hour and 0.0013 $hours^{-1}$ respectively, are between those obtained in this study and the values determined by Krzyzaniak. No indication was given of any precautions taken to prevent possible side-reactions of the anthracene.

The results of this study demonstrate that any studies involving anthracene or other dienes capable of photochemically

reacting should be carefully scrutinized and perhaps repeated. This can be further substantiated from the work of Roberts and co-workers (64) who first demonstrated that anthracene was oxidized to the photo-oxide in the presence of oxygen using silica as a catalyst. Since most studies to date have used anthracene purified chromatographically using an alumina column, the results obtained in these various studies cannot be accorded any great significance.

There have been many rate determinations of Diels-Alder reactions reported in the literature of which there are a variety of temperatures and utilizing a variety of solvents. Several general statements can be made concerning the reaction. These statements have all been verified in this study. The general reaction of all cases has been shown to be exothermic and spontaneous, with a loss of entropy while approaching equilibrium. The forward reaction is second-order and bimolecular while the reverse reaction is of the first-order.

In conclusion, from the now limited knowledge of some of the photochemical reactions and properties of anthracene and like compounds in various solvents, care should be exercised in devising experiments involving these compounds. The precision, accuracy, and significance of the eventual results will depend almost entirely upon the manner in which the experimental data is obtained.

Table 24. Comparison of Temperature Dependent Quantities for the Diels-Alder Reaction Between Anthracene and Maleic Anhydride

Investigator	Krzyzaniak (52)				Dahm (present study)			
t °C.	100	111	118	141	100	110	120	140
k_f liters/mol hour	6.5	11	16	40	54.2	67.6	85.0	126
$k_r \times 10^5$ hour^{-1}	0.67	2.76	5.90	70.8	2.76	8.91	32.2	354
$k \times 10^{-5}$	8.5	4.0	2.6	0.62	19.6	7.59	2.64	0.354
ΔF^o kcal/mol	-10.1	-9.7	-9.6	-9.0	-10.6	-10.2	-9.8	-9.1

Table 25. Comparison of the Temperature Independent Quantities for the Diels-Alder Reaction Between Anthracene and Maleic Anhydride

Investigator	Krzyzaniak (52)	Dahm (present study)
ΔE_{af} kcal/mol	14.4	6.45
ΔE_{ar} kcal/mol	35.0	35.0
ΔE_{a} kcal/mol	-20	-25.9
ΔS_{f}^{o*} entropy units	-34.7	-51.7
ΔS_{f}^{o*} entropy units	5.8	3.0
ΔS^{o} entropy units	-26	-40.8

SUMMARY

A kinetic and thermodynamic investigation of the reaction between anthracene and maleic anhydride to form cis-9,10-dihydroanthracene-9,10-endo-α,β-succinic anhydride was undertaken. The molar absorbancy indexes of anthracene in helium-saturated, boiled xylene solutions were determined in a limited range of the spectrum.

It was found that helium-saturated, boiled xylene solutions of the diene would not undergo any appreciable photochemical side-reactions.

The specific reaction rate constants for both the forward and reverse reactions were ascertained at four different temperatures and the corresponding equilibrium constants were computed from these values.

The forward reaction was found to be second-order and presumably bimolecular. Although the reverse reaction did not proceed to a sufficient extent to determine the order of the reaction directly from kinetic data, it was possible to determine the order of the reaction from the composition of the equilibrium mixtures. By this process the reverse reaction was found to be first-order.

Although it was impossible to postulate a mechanism for the reaction, the configuration of the transition state was found to be similar to the configuration of the adduct.

The kinetic and thermodynamic data determined in this investigation are summarized in Tables 26 and 27.

Table 26. Kinetic Quantities for the Diels-Alder Reaction Between Anthracene and Maleic Anhydride

Temperature degree centigrade	k_f from slope Figs. III-VI and VIII-X liters/mol hour	$k_r \times 10^5$ from slope Figs. XI-XIV $hour^{-1}$
100	54.2 ± 3.2	2.76 ± 0.06
110	67.6 ± 2.2	8.91 ± 0.10
120	85.0 ± 2.7	32.2 ± 0.6
140	126 ± 6	354 ± 13
140*	209 ± 12	----------
140**	170 ± 10	----------
140***	184 ± 8	----------

	Order	ΔE_a kcal/mol	ΔS^{o*} entropy units
Forward reaction	2	6.45 ± 0.71	-51.7 ± 9.4
Reverse reaction	1	35.0 ± 4.6	3.0 ± 0.1

*Obtained using 4.00×10^{-3} moles/liter diene and dienophile

**Obtained using an excess of diene

***Obtained using an excess of dienophile

Table 27. Thermodynamic Quantities for the Diels-Alder Reaction Between Anthracene and Maleic Anhydride

Temperature degree centigrade	K X 10^{-5} calculated as k_f/k_r	ΔF^o kcal/mol
100	19.6	-10.6 ± 0.7
110	7.59	-10.2 ± 0.3
120	2.64	- 9.8 ± 0.3
140	0.354	- 9.1 ± 0.4

$\Delta E^o \approx \Delta H^o$ = -25.9 ± 4.1 kcal/mol

ΔS^o = -40.8 ± 6.5 entropy units

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